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Calculation of the Equilibrium Composition of Systems of Many Constituents¹

STUART R. BRINKLEY, JR.²

Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania

A computational procedure is developed for the calculation of the composition at chemical equilibrium of systems of many constituents. The general equations are applied to homogeneous systems and to homogeneous systems which exist in the presence of a single additional pure phase. A brief discussion is given of appropriate numerical methods of computation.

INTRODUCTION

THE calculation of the composition of a system at chemical equilibrium is easily carried out when there is only a single reaction to be considered. In this case, the concentrations of each constituent can be related to a single variable, "the degree of reaction," and the solution of the mass action equation is straightforward. Difficulties are encountered if this method is extended to a consideration of two simultaneous equilibria, and when the number of such simultaneous equilibria becomes large, the ordinary methods become very laborious.

There exists a need for a systematic procedure designed to provide a method for writing down the necessary relations in that form which is best suited to numerical computation. Such a procedure is developed in the present paper. Unfortunately, in order to achieve generality for the method, it has been necessary to adopt a somewhat complicated nomenclature. However, the reader who is not repelled by the analytical statement of the method will find its application to particular systems straightforward and the numerical solution of the resulting equations systematic. In an extensive program of computations, the author has employed clerical personnel in all numerical portions of the work.

CALCULATION OF THE EQUILIBRIUM COMPOSITION

In a recent discussion³ of the conditions of equilibrium for systems of many constituents, it was shown that the number of components of a system containing s constituents is equal to

the rank c of the matrix of the subscripts to the symbols of the elements in the formulae of the substances comprising the system. The choice of component substances must conform to the requirement that the vectors defined by the array of subscripts to the elementary symbols in the formulae of the selected substances be linearly independent. The substances, $s-c$ in number, with linearly dependent formula vectors may be considered to be formed from the components by the reactions,

$$\sum_{j=1}^c \nu_{ij} Y^{(j)} = Y^{(i)}, \quad (1)$$

$i = c+1, c+2, \dots, s$, where $Y^{(i)}$ and $Y^{(j)}$ represent the molecular formulae of the i th dependent substance and the j th component, respectively, and where ν_{ij} is the coefficient to the j th independent vector in the linear relation expressing the dependence of the i th dependent vector.

In terms of these definitions, the conditions of equilibrium assume a particularly symmetrical form. At constant temperature and pressure, the conditions for chemical equilibrium take the form,

$$\mu_j^{(k)} = \lambda_j, \quad (2)$$

$$\mu_i^{(k)} = \sum_{j=1}^c \nu_{ij} \lambda_j, \quad (3)$$

$k = 1, 2, \dots, p$, $j = 1, 2, \dots, c$, $i = c+1, c+2, \dots, s$, where $\mu_i^{(k)}$ and $\mu_j^{(k)}$ are the chemical potentials in the k th phase of the i th and j th substances, respectively, the λ_j are constants which may be eliminated from Eq. (2), p is the number of phases, and where it is assumed for simplicity of notation that each substance is included in every phase.

The conservation of mass in the system re-

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²Physical Chemist, Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania.

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quires that

$$\sum_{k=1}^p \{n_j^{(k)} + \sum_{i=c+1}^s \bar{\nu}_{ji} n_i^{(k)}\} = q_j, \quad (4)$$

$j=1, 2, \dots, c$, where $\bar{\nu}_{ji} = \nu_{ij}$ and where $n_i^{(k)}$ and $n_j^{(k)}$ are the number of gram moles in the k th phase of the i th and j th substances, respectively. The quantities q_j are obtained by solution of the linear equations,

$$\sum_{j=1}^c \bar{\alpha}_{lj} q_j = Q_l, \quad (5)$$

$l=1, 2, \dots$, where $\bar{\alpha}_{lj}$ is the subscript to the symbol of the l th element in the molecular formula of the j th component and Q_l is the number of gram atoms of the l th element available to the system.

Because of their symmetry, Eqs. (2)–(4) provide the simplest basis for the calculation of the composition of the system at equilibrium.

The chemical potential in the k th phase of the j th component is related to the mole fraction $N_j^{(k)}$ of the j th component in the k th phase by

$$\mu_j^{(k)} = [\mu_j^{(k)}]^0 + RT \log N_j^{(k)} f_j^{(k)}, \quad (6)$$

where

$$N_j^{(k)} = n_j^{(k)} / n^{(k)}, \quad (7)$$

$$n^{(k)} = \sum_{j=1}^c n_j^{(k)} + \sum_{i=c+1}^s n_i^{(k)}, \quad (8)$$

and where $f_j^{(k)}$ is the activity coefficient on the mole fraction concentration scale in the k th phase of the j th component, $[\mu_j^{(k)}]^0$ is the chemical potential of the j th component in the k th phase at the standard state of unit activity, and $n^{(k)}$ is the total number of moles in the k th phase. Similar definitions apply for the dependent substances.

A *representative phase* may be selected for each substance of the system. The representative phases for the j th component and i th dependent substance may be denoted, respectively, by the indices k_j and k_i . Introducing for simplicity, the abbreviations,

$$N_j^{(k_j)} = x_j, \quad N_i^{(k_i)} = x_i,$$

and employing the usual definitions and methods of thermodynamics, Eqs. (2), (3), and (6) lead

to the relations,

$$N_j^{(k)} = a_{jk} x_j, \quad (9)$$

$$N_i^{(k)} = a_{ik} x_i, \quad (10)$$

$$x_i = b_i \prod_{j=1}^c x_j^{\nu_{ij}}, \quad (11)$$

$k=1, 2, \dots, p$, $j=1, 2, \dots, c$, $i=c+1, c+2, \dots, s$, where

$$a_{jk} = K_{j^{(k, k_j)}} f_j^{(k_i)} / f_j^{(k)}, \quad (12)$$

$$b_i = K_i \prod_{j=1}^c [f_j^{(k_j)}]^{\nu_{ij}} / f_i^{(k_i)}. \quad (13)$$

It may be noted that $a_{jk} = 1$ when $k = k_j$. If the j th substance is excluded *a priori* from the k th phase, then $a_{jk} = 0$. The thermodynamic equilibrium constant $K_{j^{(k, k_j)}}$ for the distribution of the j th component between the k th and k_j th phases, is defined by

$$RT \log K_{j^{(k, k_j)}} = [\mu_j^{(k_j)}]^0 - [\mu_j^{(k)}]^0. \quad (14)$$

In a similar manner, a_{ik} is related to a distribution equilibrium constant for the i th dependent substance. The thermodynamic equilibrium constant K_i for the reaction

$$\sum_{j=1}^c \nu_{ij} [Y^{(j)}]_{k_j} = [Y^{(i)}]_{k_i},$$

is defined by

$$RT \log K_i = \sum_{j=1}^c \nu_{ij} [\mu_j^{(k_j)}]^0 - [\mu_i^{(k_i)}]^0. \quad (15)$$

If Eqs. (7) to (10) are combined with Eq. (4), there are obtained the relations,

$$q_j - x_j \sum_{k=1}^p a_{jk} n^{(k)} - \sum_{i=c+1}^s \bar{\nu}_{ji} x_i \sum_{k=1}^p a_{ik} n^{(k)} = F_j(x_1, \dots, x_j, \dots, x_c; n^{(1)}, \dots, n^{(k)}, \dots, n^{(p)}) = 0, \quad (16)$$

$j=1, 2, \dots, c$. If Eqs. (9) and (10) are combined with the identity relations between mole fractions for each phase, there are obtained the additional relations,

$$1 - \sum_{j=1}^c x_j a_{jk} - \sum_{i=c+1}^s x_i a_{ik} = G_k(x_1, \dots, x_j, \dots, x_c) = 0, \quad (17)$$

$k=1, 2, \dots, p$. In view of the relations between the x_i and the x_j which are expressed by Eqs. (11), Eqs. (16) and (17) consist of $c+p$ relations between the variables $x_1, x_2, \dots, x_c, n^{(1)}, n^{(2)}, \dots, n^{(p)}$. If these equations can be solved simultaneously, the complete solution for the composition of the system can then be obtained at once by the use of Eqs. (9) to (11).

It is not usually feasible to seek a literal solution of these equations, and it is, therefore, necessary to employ an iterative procedure. As a first approximation, Eqs. (16) and (17) are solved with neglect of the dependence of the activity coefficients on the composition, and the quantities a_{jk} , a_{ik} , and b_i are evaluated either with activity coefficients corresponding to approximate values of the concentrations of the several constituents, or, in the absence of such information, with activity coefficients set equal to unity corresponding to the assumption that the phases are ideal. The results of the first approximate solution are then used to evaluate improved values of the coefficients, and these in turn are employed in a second solution of Eqs. (16) and (17) to obtain second approximate values of the concentrations. This process, which may be called the *primary iteration*, is continued until the difference between successive approximations to every variable is negligibly small. If the phases may be considered to be ideal, the primary iteration reduces to a single step.

In each step of the primary iteration, the solution of Eqs. (16) and (17) must be obtained by a series of successive approximations, which may be called the *secondary iteration*. The Newton-Raphson⁴ method is well suited to this stage of the calculation. If the functions F_j and G_k are expanded in a Taylor series about an approximate set of values of the variables with neglect of terms involving derivatives of second and higher orders, there results a set of $c+p$ linear equations which can be compactly represented in the notation of matrices by

$$\left[\begin{array}{c|c} A_{jj'}^{(r)} & B_{jk'}^{(r)} \\ \hline \bar{B}_{kj'} & 0 \end{array} \right] \left[\begin{array}{c} h_{j'}^{(r)} \\ \hline g_{k'}^{(r)} \end{array} \right] = \left[\begin{array}{c} F_j^{(r)} \\ \hline G_k^{(r)} \end{array} \right], \quad (18)$$

where the r th and $(r+1)$ th approximations to

the composition are related by

$$x_j^{(r+1)} = x_j^{(r)}(1 + h_j^{(r)}), \\ [n^{(k)}]^{(r+1)} = [n^{(k)}]^{(r)} + g_k^{(r)},$$

and where the elements of the submatrices are given by

$$A_{jj'} = x_j \delta_{jj'} + \sum_{k=1}^p a_{jk} n^{(k)} \\ + \sum_{i=c+1}^s \bar{v}_{ji} \bar{v}_{j'} x_i \sum_{k=1}^p a_{ik} n^{(k)}, \quad (19)$$

$$B_{jk} = x_j a_{jk} + \sum_{i=c+1}^s \bar{v}_{ji} x_i a_{ik}, \quad B_{kj} = B_{jk}, \quad (20)$$

$k, k'=1, 2, \dots, p, j, j'=1, 2, \dots, c$. The x_i are related to the x_j by Eqs. (11), and $\delta_{jj'}$ is the Kronecker delta. The functions F_j and G_k are defined by Eqs. (16) and (17), and the superscript r indicates that the quantity to which it refers is to be evaluated with the r th approximation to the composition of the system.

Two examples will suffice to illustrate the application of Eqs. (18) to particular systems. If the system exists in a single phase, the elements of the submatrix $A_{jj'}$ are given by

$$A_{jj'} = n_j \delta_{jj'} + \sum_{i=c+1}^s \bar{v}_{ji} \bar{v}_{j'} m_i, \quad (21)$$

and the submatrices B_{jk} and \bar{B}_{kj} become column and row matrices, respectively, with elements

$$B_j = \bar{B}_j = N_j + \sum_{i=c+1}^s \bar{v}_{ji} N_i. \quad (22)$$

If component $Y^{(1)}$ exists in a pure phase which is designated by the index σ and not in any other phase, and if all other constituents exist in a single phase designated by the index γ then $G_\sigma^{(r)} = 0$ for every r and it is easy to show by the combination of rows of the augmented matrix that Eqs. (18) for this case reduce to $h_1^{(r)} = 0$ for every r , and

$$\left[\begin{array}{cc|c} A_{1j'}^{(r)} & 0 & 1 \\ A_{jj'}^{(r)} & B_{j\gamma}^{(r)} & 0 \\ \hline \bar{B}_{\gamma j'}^{(r)} & 0 & 0 \end{array} \right] \left[\begin{array}{c} h_{j'}^{(r)} \\ \hline g_\gamma^{(r)} \end{array} \right] = \left[\begin{array}{c} F_1^{(r)} \\ \hline F_j^{(r)} \\ \hline G_\gamma^{(r)} \end{array} \right], \quad (23)$$

$j, j'=2, 3, \dots, c$. The matrix elements may be found from Eqs. (19) and (20) with the substitu-

⁴ J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, 1930), pp. 178, 187.

tions, $a_{1\sigma} = a_{j\gamma} = a_{i\gamma} = 1$, $a_{1\gamma} = a_{j\sigma} = a_{i\sigma} = 0$. If component $Y^{(1)}$ is present in unlimited excess, then $F_1 = \infty$. In this case, Eqs. (23) may be written in the form,

$$\begin{bmatrix} A_{jj'}^{(r)} & B_{j\gamma}^{(r)} \\ \bar{B}_{\gamma j'}^{(r)} & 0 \end{bmatrix} \begin{bmatrix} h_{j'}^{(r)} \\ g_{\gamma}^{(r)} \end{bmatrix} = \begin{bmatrix} F_j^{(r)} \\ G_{\gamma}^{(r)} \end{bmatrix}. \quad (24)$$

DISCUSSION

Criteria for that choice of components and representative phases which results in the most rapid convergence of the secondary iteration can be developed from the remainders to the two-term Taylor series expansions of the functions F_j and G_k . However, the resulting expressions are too cumbersome for practical utility, and in practice the convergence will be found to be satisfactory if representative phases are selected so as to minimize the sets of quantities a_{jk} and a_{ik} , $k = 1, 2, \dots, p$, for each i and j , and if the components are selected so as to minimize the set of quantities b_i , $i = c+1, c+2, \dots, s$.

Equations (18) are conveniently solved by matrix methods, of which that of Crout⁵ is particularly well adapted to machine computation. When, at some stage in the secondary iteration, the residuals $F_j^{(r)}$ and $G_k^{(r)}$ become fairly small, an appreciable saving of time results if the coefficients $A_{jj'}^{(r)}$, $B_{jk'}^{(r)}$ and $\bar{B}_{kj'}^{(r)}$ are retained for all subsequent steps in the iteration.⁶ Although the number of steps remaining is thereby increased, the amount of computation in each step is greatly reduced, particularly if the Crout method of reduction of the matrix is employed. When some of the a_{jk} , a_{ik} , or b_i are much larger than the others, it is frequently advantageous to obtain a preliminary solution of Eqs. (18) with neglect of the coefficients which are relatively small. The solution can then be completed in the manner indicated above with constant values of the elements of the square matrix.

⁵ P. D. Crout, *Trans. A.I.E.E.* **60**, 1235 (1941).

⁶ E. T. Whittaker and G. Robinson, *The Calculus of Observations* (Blackie and Son, Ltd., London and Glasgow, 1929), second edition, p. 90.