A CONTRIBUTION TO THE SIMULTANEOUS CHEMICAL AND PHASE EQUILIBRIUM CALCULATION

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Received January 19th, 1978

Some problems are treated in detail which are encountered during calculating the equilibrium composition in heterogeneous reacting systems with respect to the minimum of the total Gibbs free energy.

The calculation of the equilibrium composition in a mixture of ideal gases at constant temperature and pressure by minimizing the total Gibbs free energy of the system[1] had indicated a qualitatively new way to the solution of chemical equilibria. This method, originally developed only for an ideal gaseous phase, received immediately a wide attention and several authors extended its applications also to heterogeneous[2-5] and nonideal gaseous systems[6]. All of these methods are based on the minimization of the Gibbs free energy by the method of Lagrange multipliers with the use of computers.

The calculation methods outlined have not yet been applied to a wider extent in calculations of reacting heterogeneous systems, which are being solved solely by methods based on equilibrium constants[7-11].

In any application of the Gibbs phase law to calculations of the chemical composition of an arbitrary heterogeneous system, a careful analysis of the system is necessary. Above all one must determine the number of independent components from the total number of all reacting constituents present in the system, which then determines the number of degrees of freedom in the system. The determination of the number of independent components then also limits the number of phases which can exist in the given system. In some practical applications this limitation is solved by assuming that all condensed constituents form either one phase or an ideal solution.

The calculation of the equilibrium composition in heterogeneous systems by the White[1] resp. Boynton[3] method is based on the assumption that there can exist only one solution at a given temperature and pressure. However, it appears that the minimum of the total Gibbs free energy of the system investigated need not correspond with the equilibrium state. The result of the solution, *i.e.*, the minimum,

can be either a local minimum corresponding to a metastable state or the absolute minimum and then the solution actually corresponds to the thermodynamic equilibrium[12]. So far then, only such systems are being solved, which are composed of the ideal gaseous phase[13] and ideal solutions[14].

The calculation of any heterogeneous system requires a careful analysis of physical states in which the components present should be considered. The solution proposed, *e.g.*, by Boynton[3] leads to calculations in which the components are considered in different phases and the result with the lowest total Gibbs free energy is taken as correct. It appears, however, that – with respect to the general definition of the phase and to the dependence of the Gibbs free energy of a component in the system on its mole fraction – this method is rather uncertain. Methods, which employ Lagrange multipliers for minimizing the Gibbs free energy, are determined for finding local extremes. It appears that some systems exhibit no such local extremes, but that there is a system composition with a minimum of the total Gibbs free energy.

Let us consider a system at a constant temperature and pressure, containing N components $S_1, S_2, \ldots, S_N$ divided into h phases ($N > 1, h > 0$). Each component in this system can be expressed through the basic components $Z_1, Z_2, \ldots, Z_M$ as

$$S_i = \sum_{j=1}^{M} a_{ij} Z_j , \quad i = 1, 2, \ldots, N .$$

The mass amount of the basic component Z_j in the system is equal to b_j. Thus, the system is described by the basic components $Z_1, Z_2, \ldots, Z_M$, numbers $b_1, b_2, \ldots, b_M$ and the matrix

$$\mathbf{A} = [a_{ij}] \quad i = 1, 2, \ldots, N ; \quad j = 1, 2, \ldots, M .$$

The basic components can be selected so that the rank of matrix **A** will be M. Let n_i denote the mass amount of component S_i in the system, then the M folowing mass balance conditions are satisfied in this system

$$\sum_{i=1}^{N} a_{ij} n_i = b_j , \quad j = 1, 2, \ldots, M . \qquad (I)$$

Without any loss of generality it can be assumed that the components $S_1, S_2, \ldots, S_{N_1}$ are in the first of the phases considered, the components $S_{N_1+1}, S_{N_1+2}, \ldots, S_{N_2}$ are in the second phase, *etc.*, and finally the components $S_{N_{h-1}+1}, S_{N_{h-1}+2}, \ldots, S_{N_h}$ are in the h-th phase ($N_h = N$). The determination of the equilibrium composition in the system is equivalent to finding non-negative numbers $n_1, n_2, \ldots, n_N$ which would minimize the total Gibbs free energy of the system, $F(n_1, n_2, \ldots, n_N)$, and satisfy conditions (I). The total Gibbs free energy of the system is

$$F(n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} f_i(n_{N_{k-1}+1}, n_{N_{k-1}+2}, \ldots, n_{N_k}) ,$$

where f_i is the energy of the i-th component in the k-th phase

$$f_i(n_{N_{k-1}+1}, n_{N_{k-2}+2}, \ldots, n_{N_k}) = n_i \left(c_i + \ln \frac{n_i}{n^k} \right) \quad \text{for} \quad n_i > 0$$

$$c_i = \frac{1}{R} \left(\frac{G^0 - H_0^0}{T} \right)_i + \frac{1}{RT} (\Delta H_0^0)_i + t_i (\ln P - 11{\cdot}52609) ,$$

values of $-[(G^0 - H_0^0)/T]_i$, $(\Delta H_0^0)_i$ are tabulated, $t_i = 1$ for components in the gaseous phase, $t_i = 0$ for components in other phases.
P is the total pressure in Pa and

$$n^k = n_{N_{k-1}+1} + n_{N_{k-1}+2} + \ldots n_{N_k} .$$

In view of the relation

$$\lim_{n_i \to 0} n_i \ln \frac{n_i}{n^k} = 0 ,$$

it is possible to set $f_i = 0$ for $n_i = 0$.

Consequently, in determining the equilibrium composition of a multicomponent multiphase system at constant temperature and pressure we are searching for a constrained minimum of the function F with the variables $n_1, n_2, \ldots, n_N$, which satisfy M conditions (*1*). These conditions are independent; it means that $M \leqq N$, otherwise the rank of matrix **A** could not be equal to M. As long as $M = N$, the variables $n_1, n_2, \ldots, n_N$ are determined unambiguously by conditions (*1*).

Now let us examine conditions (*1*) in more detail. By using these conditions we can express M variables through the other $N - M$ variables; these M variables are dependent, the others independent variables. Dependent variables cannot be chosen as arbitrary M variables, but they must be selected in such a manner that the rank of the matrix of coefficients a_{ij} on the left-hand side of conditions (*1*), with independent variables transferred to their right-hand side, be equal to M. Let $n_{s_N}, n_{s_{N-1}}, \ldots, n_{s_{N-M+1}}$ be the dependent and $n_{s_1}, n_{s_2}, \ldots, n_{s_{N-M}}$ independent variables, where $s_1, s_2, \ldots, s_N$ is a suitable permutation of numbers $1, 2, \ldots, N$. By employing conditions (*1*) we can express the dependent variables as linear functions of the independent variables

$$\begin{aligned} n_{s_N} &= L_N(n_{s_1}, n_{s_2}, \ldots, n_{s_{N-M}}) , \\ n_{s_{N-1}} &= L_{N-1}(n_{s_1}, n_{s_2}, \ldots, n_{s_{N-M}}) \\ n_{s_{N-M+1}} &= L_{N-M+1}(n_{s_1}, n_{s_2}, \ldots, n_{s_{N-M}}) . \end{aligned} \qquad (2)$$

Since the variables $n_1, n_2, \ldots, n_N$ must be non-negative, the set of N linear inequalities with the variables $n_{s_1}, n_{s_2}, \ldots, n_{s_{N-M}}$

$$L_i \geqq 0\,, \quad i = N, N-1, \ldots, N-M+1\,;$$

$$n_i \geqq 0\,, \quad i = s_1, s_2, \ldots, s_{N-M}$$

determines the definition region D of the function $\bar{F}(n_{s_1}, n_{s_2}, \ldots, n_{s_{N-M}})$, which is the total Gibbs free energy of the system. The function $\bar{F}$ is obtained from the function $F(n_1, n_2, \ldots, n_N)$, in which the dependent variables are replaced with the right-hand sides of Eqs (*2*).

The definition region D is a closed set, elements of set D are $(N - M)$-tuples of mass amounts of the components $S_{s_1}, S_{s_2}, \ldots, S_{s_{N-M}}$. The function $\bar{F}$ is continuous on D, inside D it has continuous partial derivatives of the first order; consequently, $\bar{F}$ assumes on D its highest and lowest value. As regards the minimum of the function $\bar{F}$, there are two possibilities:

I. *The minimum of $\bar{F}$ is a local extreme.* In this case, the numbers $n_{s_1}, n_{s_2}, \ldots, n_{s_{N-M}}$ which minimize the function $\bar{F}$, are the solution to the set of the $N - M$ equations

$$\partial \bar{F}/\partial n_i = 0\,, \quad i = s_1, s_2, \ldots, s_{N-M} \tag{3}$$

and the remaining variables $n_{s_N}, n_{s_{N-1}}, \ldots, n_{s_{N-M+1}}$ are determined from Eqs (*2*). The equations in set (*3*) are nonlinear and, before solving them, the dependent variables must be expressed through independent ones according to relations (*2*). Set (*3*) can be solved by a method of subsequent approximations and the first approximation can be an arbitrary point of set D.

Another method for determination the equilibrium composition can be the method[1-3,5] leading to a set of $M + h$ linear equations, which is being solved several times until a required accuracy of the solution has been reached. The first approximation to the required solution must be selected in such a manner so that the mass balance conditions (*1*) may be satisfied.

Example

A system with the basic components $Z_1 = \mathrm{Cu}$, $Z_2 = \mathrm{Cl}$, $Z_3 = \mathrm{H}$, numbers $b_1 = 2$, $b_2 = 2$, $b_3 = 2$, matrix **A**

$$\mathbf{A} = \begin{bmatrix} 1 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \\ 0 & 1 & 1 \end{bmatrix}$$

$T = 800$ K; $P = 0{\cdot}1$ MPa. Each of the first two components forms an individual solid phase, the latter two a gaseous phase. The mass balance equations

$$\begin{aligned} n_1 + n_2 &= 2 \\ n_1 + n_4 &= 2 \\ 2n_3 + n_4 &= 2 \end{aligned}$$

can be used for expressing n_2, n_3 and n_4 through n_1

$$\begin{aligned} n_2 &= 2 - n_1 , \\ n_3 &= \tfrac{1}{2} n_1 , \\ n_4 &= 2 - n_1 . \end{aligned}$$

Thus, the total Gibbs free energy of the system is a function of one variable n_1.

$$\bar{F}(n_1) = 2(c_2 + c_4) + n_1 \left(c_1 - c_2 - \frac{c_3}{2} - c_4 \right) + \frac{n_1}{2} \ln \frac{n_1}{4 - n_1} + (2 - n_1) \ln \frac{4 - 2n_1}{4 - n_1} .$$

The definition region of $\bar{F}(n_1)$ is the interval $0 \leqq n_1 \leqq 2$. The dependence of the function $\bar{F}$ on n_1 is illustrated in Fig. 1. The constants c_1, c_2, c_3 and c_4 were calculated from tabulated data[15]. It is obvious from this figure that $\bar{F}(n_1)$ reaches a minimum at $n_1 \approx 0{\cdot}7$. In this case the Boynton method[2] gave $n_1 = 0{\cdot}69923$.

II. $\bar{F}$ *assumes its lowest value at the boundary of set* D. This situation will arise with certainty if either F or $\bar{F}$, which is identical, is a linear function. The function $\bar{F}$ is linear if and only if each of the phases considered contains only one component, *i.e.*, $h = N$. A simple example is represented by a system containing one substance in two or generally three phases.

Example

A system formed by one substance in three phases at constant temperature and pressure is described by one basic component Z_1, which is the substance considered. The mass amount of this substance can be arbitrary, *e.g.*, $b_1 = 1$, the matrix **A**

$$\mathbf{A} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$$

The component S_1 is Z_1 in the gaseous phase, S_2 is Z_1 in the liquid phase and S_3 is Z_1 in the solid phase. The mass balance condition is

$$n_1 + n_2 + n_3 = 1 . \qquad (4)$$

The total Gibbs free energy of the system is

$$F(n_1, n_2, n_3) = f_1(n_1) + f_2(n_2) + f_3(n_3)$$
$$= n_1 c_1 + n_2 c_2 + n_3 c_3 .$$

Condition (4) can be employed for expressing, *e.g.*, n_3 through n_1 and n_2

$$n_3 = 1 - n_1 - n_2 .$$

The function $\bar{F}$ is obtained by replacing n_3 in F

$$\bar{F}(n_1, n_2) = n_1(c_1 - c_3) + n_2(c_2 - c_3) + c_3 .$$

The inequality $n_3 \geqq 0$, which is equivalent with the inequality $1 \geqq n_1 + n_2$, must be satisfied. This inequality, together with the inequalities $n_1 \geqq 0$, $n_2 \geqq 0$, determines the definition region D of the function $\bar{F}$ with variables n_1, n_2. The region D in variables n_1, n_2 is given by the area bounded by the axes and the straight line $n_1 + n_2 = 1$.

The function $\bar{F}$ is linear on D and it is also linear on sections which form the boundary of set D. For locating the minimum of the function $\bar{F}$ at the boundary of set D, values of $\bar{F}$ at vertices of set D are of decisive importance. It holds

$$\bar{F}(1, 0) = c_1 ; \quad \bar{F}(0, 1) = c_2 ; \quad \bar{F}(0, 0) = c_3 .$$

Values of the constants c_1, c_2, c_3 depend on the substance, temperature and pressure. Let i, j, k be a suitable permutation of numbers 1, 2, 3. Three cases are now possible.

1) $c_1 \neq c_2$, $c_1 \neq c_3$, $c_2 \neq c_3$; $c_i = \min(c_1, c_2, c_3)$. According to the above discussed properties of the function $\bar{F}$ and to relation (4), the equilibrium composition is given by

$$n_i = 1 , \quad n_j = n_k = 0 .$$

2) $c_i = c_j$, $c_i \neq c_k$

a) $c_k < c_i$.

$$n_k = 1, \; n_i = n_j = 0.$$

b) $c_k < c_i$.

$$n_i = a, \; n_j = 1 - a, \; n_k = 0$$

where a is an arbitrary number from the interval $0 \leqq a \leqq 1$.

3) $c_1 = c_2 = c_3$

$\bar{F}$ is constant on D, which means that n_1, n_2 is an arbitrary pair from set D, n_3 is determined from *(4)*.

Another case in which $\bar{F}$ reaches its minimum at the boundary of set D is a system whose total Gibbs free energy has no local minimum, *i.e.*, the case for which set *(3)* or the set of equations in the method[1,4,3] possesses no solution in the set D. Thus, in this case the minimum of $\bar{F}$ lies at the boundary of set D.

Example

A system with the basic components Z_1 = Ag, Z_2 = Cu, Z_3 = Cl, Z_4 = H and numbers $b_1 = 2$, $b_2 = 2$, $b_3 = 4$, $b_4 = 4$. The matrix is

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 2 \end{bmatrix}$$

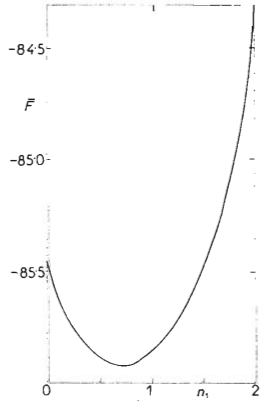

FIG. 1

The Dependence of the Function $\bar{F}$ on n_1(Cu) in the System 2 CuCl + H_2 at 800 K and 0·1 MPa

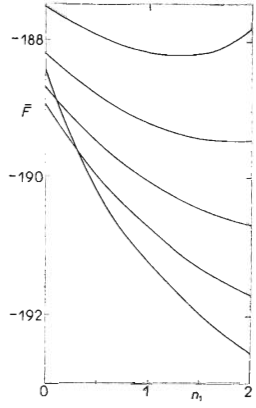

FIG. 2

The Dependence of the Function $\bar{F}$ on n_1(Ag) and n_2(Cu) in the System 2 AgCl + 2 CuCl + 2 H_2 at 600 K and 0·1 MPa

$T = 600$ K; $P = 0{\cdot}1$ MPa. Each of the first four components forms an individual solid phase, the last two components form a gaseous phase.

The mass balance conditions

$$\begin{aligned} n_1 + n_3 &= 2 \\ n_2 + n_4 &= 2 \\ n_3 + n_4 + n_5 &= 4 \\ n_5 + 2n_6 &= 4 \end{aligned}$$

can be used to express n_3, n_4, n_5, n_6 through n_1 and n_2 as

$$\begin{aligned} n_3 &= 2 - n_1 \\ n_4 &= 2 - n_2 \\ n_5 &= n_1 + n_2 \\ n_6 &= 2 - \tfrac{1}{2}(n_1 + n_2) \end{aligned}$$

Consequently, the total Gibbs free energy of the system is a function of two variables n_1, n_2

$$\begin{aligned} \bar{F}(n_1, n_2) = {} & 2(c_3 + c_4 + c_5) + n_1(c_1 - c_3 + c_5 - \tfrac{1}{2}c_6) \\ & + n_2(c_2 - c_4 + c_5 - \tfrac{1}{2}c_6) + (n_1 + n_2)\ln(n_1 + n_2) \\ & + [2 - \tfrac{1}{2}(n_1 + n_2)]\ln[2 - \tfrac{1}{2}(n_1 + n_2)] \\ & - [2 + \tfrac{1}{2}(n_1 + n_2)]\ln[2 + \tfrac{1}{2}(n_1 + n_2)] . \end{aligned}$$

The definition region of the function $\bar{F}(n_1, n_2)$ is the square $0 \leqq n_1 \leqq 2$, $0 \leqq n_2 \leqq 2$ in the n_1, n_2 coordinate plane. The dependence of the function $\bar{F}$ in n_1 is illustrated in Fig. 2 for several values of n_2. The constants $c_1, c_2, \ldots, c_6$ were calculated from tabulated data[15,16]. It is obvious from this figure that $\bar{F}(n_1, n_2)$ reaches its minimun at $n_1 = 2$, $n_2 = 0$. Thus, the equilibrium composition is:

$$n_1 = 2\,, \quad n_2 = 0\,, \quad n_3 = 0\,, \quad n_4 = 2, \quad n_5 = 2\,, \quad n_6 = 1\,.$$

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Translated by K. Hlavatý.