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Note on the Conditions of Equilibrium for Systems of Many Constituents[1]

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An analytical criterion is given for the choice of independent components. An inclusive discussion of equilibrium in systems of many constituents is thereby achieved. By reason of symmetry, the resulting conditions are particularly suited to form the basis of a calculation of the equilibrium composition of the system.

IT is well known, and has been clearly stated by Gibbs,[3] that the components selected from a system containing many constituents for describing the composition of the system must be independent and sufficient in number to describe the composition completely; however, it is not customary, to provide an analytical criterion for that choice. Such a criterion is developed in the present communication. In systems containing comparatively few constituents, a proper choice of components is usually intuitively obvious, but in more complicated systems, the criterion has a practical utility.

In terms of this criterion, the discussion in the manner of Gibbs[4] of the conditions for equilibrium of such systems becomes particularly simple and inclusive. The conditions formulated are found to possess a high degree of symmetry and to be especially well suited to form the basis for calculating the concentrations of the several constituents in the different phases of the system at equilibrium.

THE COMPONENTS

The number of constituents of any system depends upon the accuracy with which it is desired to describe its composition. The constituents to be considered must be chosen *a priori*, and this choice will usually imply the neglect of certain equilibria that may be expected to exert a negligible effect on the composition of the system at equilibrium.

Consider a closed system containing s different substances, which are assumed to be in chemical equilibrium. The molecular formula of the ith substance may be represented by

$$Y^{(i)} = X_{\alpha_{i1}}{}^{(1)} \cdots X_{\alpha_{il}}{}^{(l)} \cdots X_{\alpha_{im}}{}^{(m)}, \qquad (1)$$

$i=1, 2, \cdots s$, where $X^{(l)}$ is the symbol of the lth element, α_{il} is the subscript (which may be zero) to this symbol in the formula of the ith substance, and m is the total number of elements represented in the system. For every i, the array of subscripts α_{il}, $l=1, 2, \cdots m$, may be said to define a vector,

$$y_i = (\alpha_{i1}, \cdots \alpha_{il}, \cdots \alpha_{im}), \qquad (2)$$

which may be called the *formula vector* of substance i. If the rank of the matrix of the vector elements α_{il} is c, it follows from a well-known theorem of algebra[5] that there are c linearly independent vectors, and if $c<s$[6] there are $s-c$ linearly dependent vectors which may be expressed as linear combinations of the independent vectors. It may be assumed that the independent vectors are designated by the values 1, 2, $\cdots c$ of their index. Then the dependent vectors may be expressed as linear combinations of the form,

$$\sum_{j=1}^{c} \nu_{ij} y_j = y_i, \qquad (3)$$

$i=c+1, c+2, \cdots s$. To Eq. (3) there correspond $s-c$ conceivable chemical reactions,

$$\sum_{j=1}^{c} \nu_{ij} Y^{(j)} = Y^{(i)}, \qquad (4)$$

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[3] *Collected Works of J. Willard Gibbs* (Longmans, Green and Company, New York and London, 1928), Vol. 1, p. 63.
[4] Reference 3, pp. 63–82.
[5] See, for example, M. Bôcher, *Introduction to Higher Algebra* (The Macmillan Company, New York, 1907), Chap. III.
[6] Note that $c \leqslant m$ if $m \leqslant s$, or that $c \leqslant s$ if $m \geqslant s$.

resulting in the formation from the c substances with linearly independent formula vectors of the $s-c$ substances with linearly dependent formula vectors. It follows that the specification of c substances such that their formula vectors are linearly independent is sufficient for a description of the composition of the system. Therefore, the number of components of the system equals the rank c of the matrix of the subscripts to the symbols of the elements in the formulae of the substances comprising the system.[7] It may be noted that the choice of independent vectors is not, in general, unique, and that, in consequence, the choice of c substances as components and the expression of the remaining $s-c$ substances as products of reactions involving only the chosen components is usually not unique.

THE CONDITIONS FOR EQUILIBRIUM

The discussion of equilibrium in systems of many constituents assumes a particularly simple and symmetrical form in terms of the definitions that have been introduced. We consider the general case where the s substances are distributed among p co-existing phases. The conservation of mass in the system as a whole requires that

$$\sum_{k=1}^{p}\{\sum_{j=1}^{c} n_j^{(k)}M_j+\sum_{i=c+1}^{s} n_i^{(k)}M_i\}=\sum_{j=1}^{c} q_jM_j, \quad (5)$$

where $n_i^{(k)}$ and $n_j^{(k)}$ are the number of gram-moles in the kth phase of the ith and jth substances, respectively, M_i and M_j are the corresponding weights of one gram-mole, and the q_j are obtained by solution of the linear equations,

$$\sum_{j=1}^{c} \bar{\alpha}_{lj}q_j=Q_l, \quad (6)$$

$l=1, 2, \cdots m$, with $\bar{\alpha}_{lj}=\alpha_{jl}$ and with Q_l denoting the number of gram-atoms of the lth element available to the system. Since mass is conserved by each of reactions (4), one may substitute

$$M_i=\sum_{j=1}^{c} \nu_{ij}M_j \quad (7)$$

into Eq. (5). On equating the coefficients of M_j, there are obtained

$$\sum_{k=1}^{p}\{n_j^{(k)}+\sum_{i=c+1}^{s} \bar{\nu}_{ji}n_i^{(k)}\}=q_j, \quad (8)$$

$j=1, 2, \cdots c$, where $\bar{\nu}_{ji}=\nu_{ij}$.

It may be noted that these results lead immediately to the phase rule. Equations (9) and (10) constitute $c(p-1)+p(s-c)=ps-c$ relations between the chemical potentials. The chemical potentials in a given phase depend upon the common values of the state variables, which we assume to be only the temperature and pressure, and, since they are homogeneous functions of degree zero in the mole numbers, upon the mole fractions of the constituents of the phase, a total (because of the identity relation between mole fractions) of $p(s-1)+2$. In order that the system of equations be compatible, it is necessary that

$$ps-c\leqslant p(s-1)+2 \text{ or } p\leqslant c+2, \quad (11)$$

which is a statement of the phase rule of Gibbs[8] for systems depending upon only two state variables.

Together with Eq. (8), Eqs. (9) and (10) provide, by reason of their symmetry, the simplest basis for calculating the concentrations at equilibrium of the several constituents of the system. In particular, if the substances are limited to a single phase, the equations become

$$\begin{aligned} &n_j+\sum_{i=c+1}^{s} \bar{\nu}_{ji}n_i=q_j, \\ &\mu_i-\sum_{j=1}^{c} \nu_{ij}\mu_j=0, \quad \nu_{ij}=\bar{\nu}_{ji} \end{aligned} \quad (12)$$

for equilibrium at constant temperature and pressure. A computational procedure utilizing these relations will be presented in a subsequent communication.

[7] Compare Gibbs, reference 3, pp. 63, 67.

[8] Gibbs, reference 3, pp. 96, 97.