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Abstract

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L. S. PALATNIK and A. I. LANDAU

A GENERALIZED FORMULATION OF THE GIBBS INEQUALITY

(Presented by Academician N. V. Belov on 26 XII 1956)

Notation: V, S, P, T denote, respectively, the volume, entropy, pressure, and temperature of the entire heterogeneous system; M_i and $\mathfrak{M}_i$ denote, respectively, the mass and chemical potential of the i-th component in the entire system; v_j, s_j, m_j denote, respectively, the specific volume, specific entropy, and mass of the j-th phase of the system; x_{ij} and μ_{ij} denote, respectively, the concentration and chemical potential of the i-th component in the j-th phase; n and r denote, respectively, the number of components and the number of phases in the system.

Any multicomponent heterogeneous system, including one in which one or several components are absent from individual phases (i.e., the solubility of these components in the given phases may be neglected), can be represented by means of the concentration matrix $\|x_{ji}\|$ $(i = 1, 2, \dots, n;\ j = 1, 2, \dots, r)$. In the analytical consideration of thermodynamic systems it is usually tacitly assumed that the rank of this matrix is maximal, i.e., that its defect $\sigma = 0$. Thus, the phase rule derived by Gibbs (^{1}) and the inequality $r \leq n + 2$ apply only to such thermodynamic systems for which $\sigma = 0$.

It is possible, however, to represent actually existing thermodynamic systems with $\sigma > 0$. Examples are systems with $\sigma = 1$ for $r \leq n$, mention of which is made in Gibbs' work (^{1}, pp. 147–148), and which were considered in greater detail by A. V. Storonkin (^{2}).

As will be seen from what follows, the case of a system with $\sigma = 1$ for $r \leq n$ is a special one, and the number of possible thermodynamic systems with $\sigma > 0$ is considerably larger. These include certain thermodynamic systems with extrema of pressure and temperature, with identical concentration composition of different phases (for example, phases at points of different concentrations, allotropic phases), certain systems in which not all components participate in individual phases, etc. The task of the present work is to clarify the regularities obeyed by thermodynamic systems with $\sigma > 0$.

It is not difficult to verify, first of all, that, irrespective of the value of σ, for any equilibrium thermodynamic system the equalities of the pressures, temperatures, and chemical potentials of the corresponding components in the phases are fulfilled, and also that the Gibbs-Duhem equations, written separately for each phase of a heterogeneous system, hold. The number of intensive thermodynamic degrees of freedom (3) for a nonclosed system can be determined both from the Gibbs-Duhem equations (1,2) and from the equalities of the chemical potentials (4–7).

If any additional conditions or constraints are imposed on a thermodynamic system, these conditions must obviously be added to the Gibbs-Duhem equations or to the equalities of the chemical potentials before the number of thermodynamic degrees of freedom of the system is calculated. In the case under consideration, such additional conditions are those associated with the equality of the defect of the matrix of concen-

···of the quantity of concentrations σ, where $\sigma \geq 0$. The equalities of the chemical potentials, together with the indicated conditions, may be written in the following form:

$$\mu_{i1}(P, T; x_{11}, \dots, x_{n1}) = \dots = \mu_{ir}(P, T; x_{1r}, \dots, x_{nr}), \qquad i = 1, 2, \dots, n; \tag{1}$$

$$x_{1j} + x_{2j} + \dots + x_{nj} = 1, \qquad j = 1, 2, \dots, r; \tag{2}$$

$$\begin{vmatrix} x_{11} & \dots & x_{1,r-\chi-\sigma} & x_{1j} \\ \dots & \dots & \dots & \dots \\ x_{r-\chi-\sigma,1} & \dots & x_{r-\chi-\sigma,r-\chi-\sigma} & x_{r-\chi-\sigma,j} \\ x_{i1} & \dots & x_{i,r-\chi-\sigma} & x_{ij} \end{vmatrix} = 0, \qquad \begin{matrix} i = r-\chi-\sigma+1, \dots, n, \\ j = r-\chi-\sigma+1, \dots, r, \end{matrix} \tag{3}$$

where χ is the greater of the numbers $r - n$ and 0, and $\det\|x_{lm}\| \neq 0$ $(l, m = 1, 2, \dots, r-\chi-\sigma)$. When $x_{uv} = 0$, the corresponding function $\mu_{uv}(P, T; x_{1v}, x_{2v}, \dots, x_{nv})$ drops out of equality (1).

Analogously to the Gibbs-Duhem equations, together with the conditions of nonmaximal rank of the concentration matrix, they will be written as follows:

$$-v_j\,dP + s_j\,dT + x_{1j}d\mathfrak{M}_1 + x_{2j}d\mathfrak{M}_2 + \dots + x_{nj}d\mathfrak{M}_n = 0, \qquad j = 1, 2, \dots, r; \tag{4}$$

$$\begin{vmatrix} x_{11} & \dots & x_{1,r-\chi-\sigma} & x_{1j} \\ \dots & \dots & \dots & \dots \\ x_{r-\chi-\sigma,1} & \dots & x_{r-\chi-\sigma,r-\chi-\sigma} & x_{r-\chi-\sigma,j} \\ x_{i1} & \dots & x_{i,r-\chi-\sigma} & x_{ij} \end{vmatrix} = 0, \qquad \begin{matrix} i = r-\chi-\sigma+1, \dots, n, \\ j = r-\chi-\sigma+1, \dots, r. \end{matrix} \tag{5}$$

In relations (1)–(3) the variables are the quantities P, T and all x_{ij}, while the chemical potentials μ_{ij} are functions of these variables. In relations (4)–(5), however, the variables are the quantities P, T and all $\mathfrak{M}_i$, while the quantities v_j, s_j and all x_{ij} are functions of these variables. In this connection, relations (3) and (5), identical in form, have different contents.

It is easy to see, however, that both relations (3) and relations (5) impose the same number of constraints on a thermodynamic system. The latter remains true also in the case where some of the indicated relations are identities.

Thus, we have written two systems of equations: the system (1)–(3) and the system (4)–(5), each of which must impose on an open thermodynamic system with $\sigma \geq 0$ the same number of conditions (constraints). It is not hard to verify that, for $\sigma \leq 2-\chi$, both indicated systems of equations do indeed, with the corresponding count, give the same number of intensive thermodynamic degrees of freedom. However, for $\sigma > 2-\chi$ the rank of the following matrix, composed of the coefficients of all differentials in relations (4), becomes nonmaximal:

$$\begin{pmatrix} -v_1 & s_1 & x_{11} & x_{21} & \dots & x_{n1} \\ -v_2 & s_2 & x_{12} & x_{22} & \dots & x_{n2} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ -v_r & s_r & x_{1r} & x_{2r} & \dots & x_{nr} \end{pmatrix}. \tag{6}$$

In connection with this, in the system (4)–(5) there appear, in comparison with the system of equations (1)–(3), additional degrees of freedom. Such a discrepancy in the number of degrees of freedom indicates the impossibility of the existence of an equilibrium thermodynamic system with $\sigma > 2-\chi$. Thus, always

$\sigma \leq 2-\varkappa$. Since, obviously, σ is a nonnegative quantity, the inequality obtained by us may be written also in the following form:

$$0 \leq \sigma + \varkappa \leq 2. \tag{7}$$

Relation (7) is a generalization of the Gibbs inequality: $r \leq n+2$, or $\varkappa \leq 2$, to the case of thermodynamic systems with $\sigma > 0$. We shall call it the matrix condition for phase equilibrium, since it contains the defect σ of the concentration matrix $\|x_{ij}\|$. The method used in deriving relation (7) is, at the same time, a new method of proving the Gibbs inequality, different from those used previously ([1,2,4–7]).

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Let us now fix in equations (1)–(3) and (4)–(5) the quantity P or T. Then the terms with dP or the terms with dT drop out of relations (4), and matrix (6) assumes the following two possible forms:

$$\begin{pmatrix} -v_1 & x_{11} & \cdots & x_{n1} \\ -v_2 & x_{12} & \cdots & x_{n2} \\ \cdot & \cdot & \cdots & \cdot \\ -v_r & x_{1r} & \cdots & x_{nr} \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} s_1 & x_{11} & \cdots & x_{n1} \\ s_2 & x_{12} & \cdots & x_{n2} \\ \cdot & \cdot & \cdots & \cdot \\ s_r & x_{1r} & \cdots & x_{nr} \end{pmatrix}. \tag{8}$$

It is easy to see that, for $\sigma \leq 1 - \varkappa$, the matrices (8) retain maximal rank and, correspondingly, the systems of equations (1)–(3) and (4)–(5), when counted, give the same number of thermodynamic degrees of freedom of a nonclosed system. For $\sigma > 1 - \varkappa$, the matrices (8) will in any case already have nonmaximal rank. In this case the systems of equations (1)–(3) and (4)–(5), when counted, will give different numbers of degrees of freedom, which indicates the impossibility of the existence of an equilibrium thermodynamic system with $\sigma > 1 - \varkappa$ when $P = \text{const}$ (or $T = \text{const}$). On the other hand, when $P \neq \text{const}$ and $T \neq \text{const}$, the case of a thermodynamic system with $\sigma + \varkappa = 2$ is possible. From comparison of the two cases it follows that, when $\sigma + \varkappa = 2$, nonvariant equilibrium must be realized in a thermodynamic system, which, when P or T is fixed, passes into overdetermination. In an analogous way (fixing in equations (1)–(3) and (4)–(5) the quantities P and T and then comparing this case with that in which $P = \text{const}$ or $T = \text{const}$) it is easy to convince oneself that, when $P \neq \text{const}$ and $T \neq \text{const}$ and $\sigma + \varkappa = 1$, monovariant equilibrium is realized in the thermodynamic system, passing, when P or T is fixed, into nonvariant equilibrium, and when both P and T are fixed–into overdetermination. We note that, in the special case of a thermodynamic system with $\sigma = 1$ and $\varkappa = 0$ (i.e., with $r \leq n$), the monovariant properties of such a system were first pointed out by A. V. Storonkin (^{2}).

In the light of the results obtained, the meaning of conditions (7) becomes clear. Evidently, it reduces to the fact that, when $\sigma + \varkappa > 2$, overdetermination arises in the thermodynamic system (in whatever fundamental equations describe the given system) even in the case when P and T of the system are not fixed in advance. By direct verification it is easy to convince oneself that, indeed, such overdetermination arises when $\sigma + \varkappa > 2$ in the system of equations (1)–(3). In particular, as is known, overdetermination arises in the system (1)–(3) when $\sigma = 0$ and $\varkappa > 2$.

Overdetermination in the system of equations (1)–(3) may in the general case be contained not in this entire system of equations, but in a definite group of relations from this system. In just the same way, nonvariant overdetermination of the variables when $\sigma + \varkappa = 2$, or monovariant overdetermination of the variables when $\sigma + \varkappa = 1$ (in both cases $P \neq \text{const}$ and $T \neq \text{const}$), may in the general case be inherent not in the entire system of equations (1)–(3), but in a definite group of relations from this system.

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With the aid of the generalized "center of gravity" rule (^{8}), it is not difficult to convince oneself that $\sigma + \varkappa = z$, where z is the number of masses of phases m_j that can vary arbitrarily

for fixed values of the quantities P, T, and M_i $(i = 1, 2, \ldots, n)$. Hence there follows the following criterion for the nonvariant and monovariant properties of a thermodynamic system: for $z = 1$ the system possesses monovariant properties, and for $z = 2$, nonvariant properties. For $z = 3, 4 \ldots$, by analogy with the preceding two cases, we would have to obtain a thermodynamic system possessing negative variance equal, respectively, to $-1, -2, \ldots$. In reality, however, for $z > 2$ a thermodynamic system cannot be realized as an equilibrium system, and "negative variance" in the mathematical sense corresponds to overdetermination in the system of equations (1)–(3). From this point of view we can further clarify in a new way the physical meaning of the matrix condition for phase equilibrium (7) (i.e., the condition $z \leq 2$). Indeed, when $\sigma + \chi = z > 2$, even specifying the basic set (3) of external parameters V, S, and all M_i, does not make it possible to determine uniquely all the masses m_j of the thermodynamic system, i.e., all its internal parameters (which include the masses m_j). On the other hand, it follows from the fundamental equations of a thermodynamic system (^{1},^{9}) that the maximum number of independent external parameters of the system is $n + 2$, and the quantities V, S, and all M_i exhaust this number. Thus, when $\sigma + \chi = z > 2$, a thermodynamic system either is essentially not uniquely resolvable, which in principle cannot be allowed, or else the fundamental equations do not fully reflect the thermodynamic system in the case under consideration, i.e., they lose their name of fundamental equations. As we see, the matrix condition for phase equilibrium (7) resolves all the difficulties that have arisen, by prohibiting the existence of equilibrium systems with $\sigma + \chi > 2$.

Kharkov State University
named after A. M. Gorky

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