

PROPERTIES OF THE GIBBS FUNCTION IN AN IDEALLY REACTING GASEOUS MIXTURE

P. VOŇKA and R. HOLUB

*Department of Physical Chemistry,
Institute of Chemical Technology, 166 28 Prague 6*

Received October 1st, 1973

Properties of the Gibbs function have been investigated for an ideal gaseous mixture in a closed reacting system with N components. A proof has been performed of the convex course of the Gibbs function as a function of reaction coordinates in the entire physical region and consequences are given which secure unambiguity of the solution for chemical equilibrium of ideal gaseous mixtures.

Methods based on the minimization of the Gibbs function have recently become widely used for determining the equilibrium composition of gaseous mixtures. In comparison with earlier methods based on the characterization of the reacting system by the equilibrium constants display these methods, firstly proposed for general use by Dantzig^{1,4}, indisputable advantages. They avoid the necessity of performing an *a priori* stoichiometric analysis, the number of equations is given by the number of elements and not by that of possible components, which leads to a relatively small number of nonlinear equations with good convergence of the solution.

A necessary condition for the convergence is that the total Gibbs function of the system considered have a single minimum in the physical region. A proof is given in the following text that the course of this function is really convex and that the problem has a unique solution in the region considered.

A closed system composed of M elements and N components, in which a chemical reaction may proceed, can be described by two basic sets of relations: balance and reaction ones. The first of them determines relative quantities of individual components at the constant total amount of each of present elements and is expressed by the relations

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

where a_{ij} is the constitution coefficient which denotes the number of gram atoms of the j -th element in the i -th component, b_j is the total number of gram atoms of the j -th element in the system and n_i is the number of moles of the i -th component. The reaction set determines the overall chemical transformation of the system by R linearly independent reactions

$$\sum_{i=1}^N \nu_{ri} A_i = 0 \quad r = 1, 2, \dots, R, \quad (2)$$

where ν_{ri} is the stoichiometric coefficient of the i -th component in the r -th reaction and A_i is the symbol for the i -th component.

The determination of chemical equilibrium in a closed system at a constant temperature and pressure is equivalent to finding a minimum in the Gibbs function, which, for an ideal mixture of ideal gases (and to a multiple of RT) has the form of

$$G = \sum_{i=1}^N n_i (c_i + \ln n_i - \ln n), \quad (3)$$

where $c_i = G_i^0/RT + \ln P$, G_i^0 is the standard molar Gibbs free energy of the i -th component. The minimum in the Gibbs function must be searched for on the set of points fulfilling equations of the material balance (1).

By connecting Eqs (2) and the relation $A_i = \sum_{j=1}^M a_{ij} B_j$, where B_j is the symbol for the j -th element, the following relation may be deduced²

$$R = N - H, \quad (4)$$

where H is the rank of the matrix of the constitution coefficients (in practical cases it usually holds $H = M$). Value R in relation (4) must be looked upon as the maximal number of linearly independent reactions which may proceed in the system. The material balance of the system may be expressed in a form which is equivalent to Eqs (1)

$$n_i = n_i^0 + \sum_{r=1}^R \nu_{ri} \xi_r \quad i = 1, 2, \dots, N, \quad (5)$$

where n_i^0 is the initial number of moles of the i -th component and ξ_r is the reaction coordinate. Let set Ω be a set of such $(\xi_1, \xi_2, \dots, \xi_R)$ that it holds $n_i = n_i^0 + \sum_{r=1}^R \nu_{ri} \xi_r > 0$ for $i = 1, \dots, N$.

We will now study properties of function $G = G(\xi_1, \xi_2, \dots, \xi_R)$ on set Ω . We will prove that function G is convex on the set, i.e. that the quadratic form of the second differential is positively definite, or

$$\sum_{s=1}^R \sum_{k=1}^R q_{sk} h_s h_k > 0 \quad (6)$$

for an arbitrary vector \mathbf{h} such that $\|\mathbf{h}\| \neq 0$, where $q_{sk} = \partial^2 G / \partial \xi_s \partial \xi_k$. In technical

practice, $d\xi_i$ is often used instead of h_i . Relation (6) is equivalent to well-known Sylvester's relations, which state that leading minors of matrix $\{q_{ij}\}$ are positive. It follows from relations (3) and (5) that

$$q_{sk} = \sum_{i=1}^N v_{si}v_{ki}/n_i - v^{(s)}v^{(k)}/n, \quad (7)$$

$$s = 1, 2, \dots, R, \quad k = 1, 2, \dots, R,$$

where $n = \sum_{i=1}^N n_i$, $v^{(p)} = \sum_{i=1}^N v_{pi}$, $p = 1, 2, \dots, R$. Substituting Eq. (7) into inequality (6) we obtain

$$\sum_{i=1}^N (\alpha_i^2/n_i) - \alpha^2/n > 0, \quad (8)$$

where

$$\alpha = \sum_{k=1}^N \alpha_k \quad \alpha_i = \sum_{p=1}^R v_{pi}h_p. \quad (9)$$

If we want to prove inequality (8), we must secure (see Appendix) that at arbitrary $n_i > 0$, $i = 1, \dots, N$ it is not possible to choose such a vector \mathbf{h} ($\|\mathbf{h}\| \neq 0$) that it holds

$$\alpha_i = \alpha n_i/n \quad i = 1, 2, \dots, N. \quad (10)$$

Substituting Eq. (9) into Eq. (10) we obtain the set of equations

$$\sum_{p=1}^R (v_{pi} - n_i v^{(p)}/n) h_p = 0 \quad i = 1, 2, \dots, N. \quad (11)$$

The solution of set (11) will be trivial ($h_1 = h_2 = \dots = h_R = 0$) only for the rank of the matrix of set (11) equal to R . The i -th row of the matrix of set (11) is equal to the difference between the i -th row of the matrix of stoichiometric coefficients and the sum of all rows of the same matrix multiplied by the number n_i/n . In view of the fact that the rank of the matrix of stoichiometric coefficients is equal to R (considering R linearly independent reactions), the rank of the matrix of set (11) is also equal to R . Relation (8) may be also proved by physical reasons. It is obvious from relations (9) and (5) that the value α_i denotes the increment in the number of moles of the i -th component. In a closed system, however, all α_i 's, $i = 1, \dots, N$ cannot have the same sign. This is in contradiction with relation (10) (also see Appendix). By this we have proved that function G is convex on the entire set Ω . As a result, function G can have at most one minimum on this set.

We still want to prove that the minimum of function G lies always inside set Ω . We must namely realize that convexity ensures only unambiguity but not existence of a minimum (*e.g.* function $\exp(x)$ is convex on $(-\infty, \infty)$, but it has no minimum on this set). It follows from Eqs (3) and (5) that

$$\partial G / \partial \xi_s = \sum_{i=1}^N v_{si}(c_i + \ln n_i/n) \quad s = 1, 2, \dots, R. \quad (12)$$

For a given value of s , *i.e.* for a given s -th reaction, at least one positive and one negative stoichiometric coefficient exist. We may let the s -th reaction proceed from its left to right side; then at least one $n_i \rightarrow 0_+$ and $\partial G / \partial \xi_s \rightarrow \infty$, because of $v_{si} < 0$. Similarly for the reaction proceeding completely from its right to left side, it holds for another $n_i \rightarrow 0_+$ and $\partial G / \partial \xi_s \rightarrow -\infty$, as $v_{si} > 0$. This proves the existence and unambiguity of the minimum on set Ω .

This property of the G -function has several consequences:

1) The ideal mixture of ideal gases cannot split into two and more phases after chemical equilibrium has been established (this is due to the convexity of the G -function).

2) The set of equations

$$\sum_{i=1}^N v_{si}(c_i + \ln n_i/n) = 0 \quad s = 1, 2, \dots, R \quad (13)$$

has just one solution $(\xi_1, \xi_2, \dots, \xi_R)$ in Ω . It may be proved easily that also the set of equations

$$\prod_{i=1}^N (n_i P/n)^{v_{si}} = K_s \quad s = 1, 2, \dots, R \quad (14)$$

has just one solution in Ω (K_s is the equilibrium constant of the s -th reaction). Taking logarithms of Eqs (14) and using the thermodynamic relation

$$RT \ln K_s = - \sum_{i=1}^N v_{si} G_i^0 \quad s = 1, 2, \dots, R \quad (15)$$

we obtain a set of equations identical with set (13). The existence and unambiguity of the solution of Eq. (14) in Ω for $R = 1$ have been proved earlier³.

Set (14), resp. (13), is a system of R equations for R unknowns. It is more advantageous to minimize the G -function at constraints expressed by material balance equations (1) than Eqs (5) during solving a complex chemical equilibrium, when the number of components, N , is large (and, consequently, the number of reactions, R , is also

large). Although both procedures are obviously entirely mathematically equivalent, the first one avoids the necessity of knowing the matrix of stoichiometric coefficients and the resulting set of equations is of the dimension equal to M , where M is the number of elements in the system. A concrete elaboration of different variants of this method is *e.g.* in^{4,5}.

APPENDIX

The inequality

$$\sum_{i=1}^N (a_i^2/n_i) - a^2/n \geq 0 \quad (16)$$

holds for all $n_i > 0$, a_i $i = 1, 2, \dots, N$, where $n = \sum_{k=1}^N n_k$ and $a = \sum_{k=1}^N a_k$. Relation (16) becomes equality just for

$$a_i/n_i = a/n \quad i = 1, 2, \dots, N. \quad (17)$$

Inequality (16) may be proved easily by searching for the minimum of the lhs of relation (16). Let us note that a necessary condition for the equality in relation (16) is that all values of a_i have the same sign.

Thanks are due to Dr A. Malijevský and Dr J. P. Novák for stimulating discussions.

REFERENCES

1. Dantzig G. B.: *Lineárne programovanie a jeho rozvoj*, p. 538. Published by SVTL, Bratislava 1966.
2. Aris R., Mah R. H. S.: *Ind. Eng. Chem., Fundam.* 2, 90 (1963).
3. Moritz P.: *Acta Chim. Acad. Sci. Hung.* 3, 421 (1953).
4. White W. B., Johnson S. M., Dantzig G. B.: *J. Chem. Phys.* 28, 751 (1958).
5. Voňka P., Holub R.: *This Journal* 36, 2446 (1971).

Translated by K. Hlavatý.