Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1961

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1961. Volume 140, No. 6

PHYSICAL CHEMISTRY

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SOME GENERAL INEQUALITIES OF CHEMICAL THERMODYNAMICS

(Presented by Academician V. N. Kondrat' ev on 3 VI 1961)

It is known that the thermodynamic equilibrium of any system occurs at the minimum of the thermodynamic potential of the system Φ (in the variables p, T) or at the minimum of the free energy F (in the variables v, T). The condition for an explicit minimum, in addition to $\delta\Phi = 0$ ($\delta F = 0$), is the requirement $\delta^2\Phi > 0$ ($\delta^2 F > 0$). The positivity of the second variation of the characteristic functions means thermodynamic stability of the system. For arbitrary reacting systems, the condition of thermodynamic equilibrium $\delta\Phi = 0$ ($\delta F = 0$) is the condition of chemical equilibrium and, for ideal gases, ultimately represents the law of mass action. As for the thermodynamic stability of such systems, in the case of ideal gases it can be proved directly (a proof for one reaction is given, for example, in ([1])). Here we shall give a proof of thermodynamic stability for arbitrary reacting systems of ideal gases, with the aim of deriving from this fact a number of general inequalities of chemical thermodynamics.

The conditions of chemical equilibrium have the form ($i = 1, 2, \dots, k$):

$$\delta\Phi = \sum_i \left(\frac{\partial\Phi}{\partial N_i}\right)_{p,T} \delta N_i = \sum_i \mu_i(p,T)\,\delta N_i = 0,$$

$$\delta F = \sum_i \left(\frac{\partial F}{\partial N_i}\right) \delta N_i = \sum_i \mu_i(v,T)\,\delta N_i = 0, \qquad (1)$$

where

$$\mu_i(p,T) = \mu_i^0(p,T) + RT\ln(N_i/N),$$

$$\mu_i(v,T) = \mu_i^0(v,T) + RT\ln N_i \qquad (2)$$

are the chemical potentials of an ideal gas in the variables p, T and v, T, respectively (the first terms in (2) do not depend on the number of moles N_i and N).

Using the representations $(s, t = 1, 2, \dots, r)$

$$\delta N_i(p,T) = \sum_s \nu_{is}\delta\alpha_s, \qquad \delta N_i(v,T) = \sum_s \nu_{is}\delta\beta_s, \tag{3}$$

which are forms of the material balance, the conditions (1) can be written otherwise:

$$\delta\Phi = \sum_{s,i} \nu_{is}\mu_i\delta\alpha_s = \sum_s \varphi_s\delta\alpha_s = 0,$$

$$\delta F = \sum_{s,i} \nu_{is}\mu_i\delta\beta_s = \sum_s f_s\delta\beta_s = 0.$$

Since the variables $\delta\alpha_s, \delta\beta_s$ are independent, $\varphi_s = f_s = 0$. Using (2) and (3), the desired second variations of the characteristic functions can be represented in the form

$$\frac{\delta^2\Phi}{NRT} = \sum_{s,t} \Phi_{s,t}\frac{\delta\alpha_s}{N}\frac{\delta\alpha_t}{N}, \qquad \frac{\delta^2 F}{NRT} = \sum_{s,t} F_{st}\frac{\delta\beta_s}{N}\frac{\delta\beta_t}{N}, \tag{4}$$

where

$$\Phi_{st} = \sum_i \frac{\nu_{is}\nu_{it}}{x_i} - \nu_s\nu_t = F_{st} - \nu_s\nu_t = \Phi_{ts}, \qquad F_{st} = \sum_i \frac{\nu_{is}\nu_{it}}{x_i} = F_{ts}. \tag{5}$$

Here $\nu_s = \sum_i \nu_{is}$ is the total stoichiometric coefficient of reaction s.

The conditions for positive definiteness of the bilinear forms (4) consist in the positivity of all principal diagonal elements and principal minors of the corresponding matrices $\|\Phi_{st}\|$ and $\|F_{st}\|$. In view of the arbitrariness of the number of reactions, it is sufficient, evidently, to prove the positivity of the principal diagonal elements and of the full determinants of the matrices $\|\Phi_{st}\|$ and $\|F_{st}\|$.

Let us introduce the characteristic matrix of our system, which, evidently, completely determines the properties of the system:

$$\|M\| = \left\| \begin{matrix} \nu_{11} & \nu_{12} & \dots & \nu_{1r} & x_1 \\ \nu_{21} & \nu_{22} & \dots & \nu_{2r} & x_2 \\ \vdots & \vdots & & \vdots & \vdots \\ \nu_{k1} & \nu_{k2} & \dots & \nu_{kr} & x_k \end{matrix} \right\|. \tag{6}$$

By direct calculation, making use of the normalization condition $\sum_i x_i = 1$, it is not difficult to show that the principal diagonal elements of the matrix $\|\Phi_{st}\|$ have the form

$$\Phi_{ss} = \frac{1}{2} \sum_{i_1, i_2} \frac{m^2_{i_1, i_2; s}}{x_{i_1} x_{i_2}} > 0,$$

where $m_{i_1, i_2; s}$ are the quadratic minors of $\|M\|$, whose elements stand at the intersections of rows with indices $i_1 \neq i_2$ and columns with indices s and $r+1$. The positivity of F_{ss} is evident. The conditions $\Phi_{ss} > 0$ and $F_{ss} > 0$ are sufficient for the thermodynamic stability of one reaction in the system and were already obtained in (1).

Let us denote by $\Delta_{i_1, i_2, \ldots, i_{r+1}}$ the minors of $\|M\|$ of rank $r+1$, consisting of rows with indices $i_1 \neq i_2 \neq \ldots \neq i_{r+1}$, and by $\delta_{i_1, i_2, \ldots, i_r}$ the minors of rank r of the first r columns and rows of $\|M\|$ with analogous indices. For the full determinants Δ and δ of the matrices $\|\Phi_{st}\|$ and $\|F_{st}\|$, the following representations, obtained by induction, hold:

$$\Delta = \frac{1}{(r+1)!} \sum_{i_1, i_2, \ldots, i_{r+1}} \frac{\Delta^2_{i_1, i_2, \ldots, i_{r+1}}}{x_{i_1} x_{i_2} \ldots x_{i_{r+1}}} > 0,$$

$$\delta = \frac{1}{r!} \sum_{i_1, i_2, \ldots, i_r} \frac{\delta^2_{i_1, i_2, \ldots, i_r}}{x_{i_1} x_{i_2} \ldots x_{i_r}} > 0.$$

The nonvanishing of at least one $m_{i_1, i_2; s}$ and $\Delta_{i_1, i_2, \ldots, i_{r+1}}$ is evident, since otherwise, in view of the fact that some ν_{is} are necessarily negative, the absurd conclusion would be obtained: some x_i are negative. The nonvanishing of at least one $\delta_{i_1, i_2, \ldots, i_r}$ follows from the condition of independence

reactions. Thus, the conditions for the positive definiteness of the forms (4) hold, and therefore the system under consideration, when at least one reaction actually proceeds, is thermodynamically stable.

The molar heat capacities have the form

$$c_p/R = \sum_i \frac{c_{p_i}}{R} x_i + \sum_i \frac{H_i}{RT} u_i, \qquad c_v/R = \sum_i \frac{c_{v_i}}{R} x_i + \sum_i \frac{U_i}{RT} v_i, \tag{7}$$

where

$$u_i = \frac{1}{N} \left(\frac{\partial N_i}{\partial \ln T} \right)_p, \qquad v_i = \frac{1}{N} \left(\frac{\partial N_i}{\partial \ln T} \right)_v.$$

Making the substitutions $u_i = \sum_s \nu_{is}\gamma_s$, $v_i = \sum_s \nu_{is}\delta_s$, we obtain for the chemical parts of the heat capacities the expressions

$$c_{p\,ch}/R = \sum_s \left(\frac{Q_{p_s}}{RT}\right)\gamma_s, \qquad c_{v\,ch}/R = \sum_s \left(\frac{Q_{v_s}}{RT}\right)\delta_s, \tag{8}$$

where $Q_{p_s} = \sum_i \nu_{is}H_i$ is the heat effect of the reaction at $p = \text{const}$; $Q_{v_s} = \sum_i \nu_{is}U_i = Q_{p_s} - \nu_{sRT}$ is that at $v = \text{const}$.

Taking logarithms, and then differentiating with respect to T at $p = \text{const}$ and at $v = \text{const}$, the equations of the law of mass action in the form

$$\prod_i N_i^{\nu_{is}} = \left(\frac{N}{p}\right)^{\nu_s} K_{p_s} = \left(\frac{V}{RT}\right)^{\nu_s} K_{p_s}, \tag{9}$$

where K_{p_s} is the equilibrium constant, we obtain systems for determining γ_s and δ_s:

$$\sum_t \Phi_{st}\gamma_t = \frac{Q_{p_s}}{RT}, \qquad \sum_t F_{st}\delta_t = \frac{Q_{v_s}}{RT}. \tag{10}$$

Here the relation $\partial \ln K_{p_s}/\partial \ln T = d\ln K_{p_s}/d\ln T = Q_{p_s}/RT$ has been used.

From (8) and (10), by virtue of the thermodynamic stability of the system proved above, we obtain the results of interest to us:

$$c_{p\,ch}/R = \sum_{s,t} \Phi_{st}\gamma_s\gamma_t > 0, \qquad c_{v\,ch}/R = \sum_{s,t} F_{st}\delta_s\delta_t > 0. \tag{11}$$

This is the first pair of general inequalities of chemical thermodynamics.*

Let us consider the quantities

$$\left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T = -\left(\frac{\partial \ln N}{\partial \ln p}\right)_T = -\sum_i p_i, \qquad \left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T = \left(\frac{\partial \ln N}{\partial \ln v}\right)_T = \sum_i q_i, \tag{12}$$

where μ is the molecular weight of the system,

$$p_i = \frac{1}{N}\left(\frac{\partial N_i}{\partial \ln p}\right)_T, \qquad q_i = \frac{1}{N}\left(\frac{\partial N_i}{\partial \ln v}\right)_T.$$

Making the substitutions $p_i = \sum_s \nu_{is}\xi_s$, $q_i = \sum_s \nu_{is}\eta_s$, we obtain

$$\left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T = -\sum_s \nu_s \xi_s, \qquad \left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T = \sum_s \nu_s \eta_s. \tag{13}$$

Taking logarithms and then differentiating equation (9) with respect to p and to v at $T = \text{const}$, we obtain systems for determining ξ_s and η_s:

$$\sum_t \Phi_{st}\xi_t = -v_s, \qquad \sum_t F_{st}\eta_t = v_s. \tag{14}$$

From (13) and (14), by virtue of the proved thermodynamic stability of the system, we obtain the results of interest to us:

$$\left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T = \sum_{s,t} = \Phi_{st}\xi_s\xi_t > 0, \qquad \left(\frac{\partial \ln \mu}{\partial \ln \rho}\right)_T = \sum_{s,t} F_{st}\eta_s\eta_t > 0. \tag{15}$$

This is the second pair of general inequalities of chemical thermodynamics.

For the inequalities (11) to hold, it is sufficient that at least one pair Q_{ps}, Q_{vs} be nonzero; for the inequalities (15) to hold, it is sufficient that at least one v_s be nonzero.

Using further the relation between Φ_{st} and F_{st}, it is not difficult to obtain the inequality

$$\left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T \left[\left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T - \left(\frac{\partial \ln \mu}{\partial \ln \rho}\right)_T\right] = \sum_{s,t} F_{st}(\xi_s + \eta_s)(\xi_t + \eta_t) > 0. \tag{16}$$

Thus, in view of (15)*,

$$0 < \left(\frac{\partial \ln \mu}{\partial \ln \rho}\right)_T < \left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T; \tag{17}$$

$$0 < \left(\frac{\partial \ln p}{\partial \ln \rho}\right)_T = \left(\frac{\partial \ln \mu}{\partial \ln \rho}\right)_T \Big/ \left(\frac{\partial \ln \mu}{\partial \ln p}\right)_T < 1. \tag{18}$$

Moreover, from the equation of state we have

$$0 < \left(\frac{\partial \ln \mu}{\partial \ln \rho}\right)_T = 1 - \left(\frac{\partial \ln p}{\partial \ln \rho}\right)_T < 1. \tag{19}$$

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* In (*) a proof is given of the positivity only of the general c_p and c_v.

The dimensionless isothermal speed of sound $(\partial \ln p / \partial \ln \rho)_T$ may be represented in another way:

$$0 < \left(\frac{\partial \ln p}{\partial \ln \rho}\right)_T = \left(\frac{\partial \ln p}{\partial \ln \rho}\right)_v \Big/ \left(\frac{\partial \ln v}{\partial \ln T}\right)_p = \frac{1 - (\partial \ln \mu / \partial \ln T)_v}{1 - (\partial \ln \mu / \partial \ln T)_p} < 1. \qquad (20)$$

It follows from (20), in particular, that when $(\partial \ln \mu / \partial \ln T)_v > 1$ one has $1 < (\partial \ln \mu / \partial \ln T)_v < (\partial \ln \mu / \partial \ln T)_p$, while when $(\partial \ln \mu / \partial \ln T)_v < 1$ one has $(\partial \ln \mu / \partial \ln T)_p < (\partial \ln \mu / \partial \ln T)_v < 1$.

Since $(c_p - c_v)/R = (\partial \ln p / \partial \ln T)_v (\partial \ln v / \partial \ln T)_p$, from (20) we obtain the estimate

$$\left[1 - \left(\frac{\partial \ln \mu}{\partial \ln T}\right)_v\right]^2 - 1 < \frac{c_{pch} - c_{vch}}{R} < \left[1 - \left(\frac{\partial \ln \mu}{\partial \ln T}\right)_p\right]^2 - 1. \qquad (21)$$

If $(\partial \ln \mu / \partial \ln T)_v < 0$, then from (21) we have $c_{pch} - c_{vch} > 0$, and, moreover,

$$\left(\frac{\partial T}{\partial v}\right)_\mu = \frac{p}{c_v}\left(\frac{\partial \mu}{\partial \ln T}\right)_v < 0, \qquad \left(\frac{\partial T}{\partial p}\right)_h = -\frac{v}{c_p}\left(\frac{\partial \mu}{\partial \ln T}\right)_p > 0.$$

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Received
2 VI 1961

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* In (?) a proof is given only of the positivity of $(\partial \ln p / \partial \ln \rho)_T$.