

USE OF GIBBS EQUATION IN IRREVERSIBLE THERMODYNAMICS. I. GIBBS AND GIBBS-DUHEM EQUATIONS AND DEFINITION OF PARTIAL QUANTITIES IN SPECIFIC VARIABLES

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The principle of local equilibrium in nonequilibrium thermodynamics of a multicomponent continuum is expressed by the Gibbs caloric equation in field variables. This equation enables to define thermodynamic specific quantities of a mixture and partial specific quantities so that the same relations apply among them as among analogous quantities in classical thermodynamics (e.g. the Gibbs-Duhem equation). However, it is not necessary to introduce the assumption of homogeneity of the system. In the special case of a homogeneous system, the mentioned relations become identical with the common equations of classical thermodynamics.

The main assumption in irreversible thermodynamics of a continuum is the principle of local equilibrium¹⁻⁷. Its formulations lie between the following two extremes: First formulation (Meixner, Reik²): An inhomogeneous continuum (the term "homogeneous" is understood as uniform, i.e. in a homogeneous system the space gradients of all quantities are zero) is divided into sufficiently small volume elements, each of which is considered as an open homogeneous system. When we express the quantities and equations of classical thermodynamics in this element in specific (intensive) variables, we can treat them as functions of coordinates and time (corresponding to the given element), i.e. as field variables. The principle of local equilibrium can then be formulated as follows: All relations among specific (intensive) quantities in a nonequilibrium heterogeneous system are the same as in an open homogeneous system described by classical thermodynamics. Hence, in a nonequilibrium system, not only the Gibbs caloric equation (expressed in specific quantities) but also the relations among partial specific quantities, the Gibbs-Duhem equation etc., apply.

Second formulation (Truesdell-Toupin⁸, § 246 f.) is typical for the field theory. To a particle of a continuum (in the sense of continuum mechanics^{7,8}), a specific internal energy is a priori attributed, which depends on a set of *a priori* chosen parameters (generally also on their past values^{9,11}). Determining these parameters and dependence can be considered in this formulation as a postulate of local equilibrium in the most general sense. Its validity can be checked, as usual in the field theory⁸, only on examining its consequences.

For most materials, processes and conditions studied by the "classical" irreversible thermodynamics of continuum¹⁻⁷, this formulation of the principle of local equilibrium is unnecessarily general. As a first approximation⁸⁻¹⁴, it is sufficient to assume that the specific internal energy depends on the same quantities in the same manner as in an open homogeneous system, i.e. on the specific entropy and a set of intensive variables of mechanic and electromagnetic character (forming a so-called "thermodynamic substate", § 246 in ref.⁸), corresponding at a given time to a given particle of the continuum.

The second formulation is obviously more plausible owing to its deductive character (the homogeneous case is a special one, in contrast to the inductive first formulation), possibility of a wide generalization (even systems far from equilibrium can be considered), simplicity and conciseness of the basic postulate (only the caloric equation and quantities involved in it are postulated, whereas in the first formulation all thermodynamic quantities and relations are postulated) and finally because this point of view of the field theory has been used already in deriving balance equations of continuum, to which the principle of local equilibrium in irreversible thermodynamics is applied.

The term "principle of local equilibrium" is not quite adequate in the second formulation, especially in the more general concept (even in the first formulation, the volume element forming an open homogeneous system need not be in, *e.g.*, chemical equilibrium: ref.⁵, § 1.23). It is better to speak about formulation of a constitutive equation⁸ for the internal energy describing sufficiently the given system under given conditions.

It can be expected intuitively that we obtain the same results on using the second formulation of the principle of local equilibrium (in the simplified form of the above-mentioned approximation) as on using the first formulation. However, Truesdell (ref.⁸, § 254, 255, 260, and ref.¹⁵) pointed out that generally this is not the case. In the second formulation of local equilibrium, based on postulation of the Gibbs caloric equation, the chemical potentials need not have their usual significance, the partial quantities must be defined *a priori* (for multicomponent continua, the starting postulates of local equilibrium are *a priori* postulated caloric equations of components) and the Gibbs–Duhem equation does not apply.

It will be shown in the present work that the mentioned conclusions are not necessary. We shall start, similar to Truesdell⁸, from the second formulation of the principle of local equilibrium by postulation of the Gibbs caloric equation for a mixture (our method does not require to postulate caloric equations of components *a priori*). We shall show that the chemical potential and partial specific quantities can be defined so that they fulfil the Gibbs–Duhem equation, and it is not necessary to speak about homogeneity of the system. In the special case of a homogeneous system these quantities and relations are identical with equally termed quantities and relations of classical thermodynamics¹⁶.

By the mentioned method, it can be achieved that the more plausible second formulation of the principle of local equilibrium in the simplified form leads to the same consequences as the first one. Owing to this agreement, the thermodynamic quantities and relations in the previous work^{17–19} (where the first formulation, partial specific quantities and the Gibbs–Duhem equation were used) can be considered as those which are defined and derived in the present work. This is consistent with the fact that the balance equations of a multicomponent continuum were postulated for mixtures¹⁷ similarly as the Gibbs caloric equation in the mentioned second formulation of the local equilibrium principle (in contrast to Truesdell and Toupin⁸).

Gibbs Caloric Equation, Definitions of Chemical Potential and Thermodynamic Pressure

We shall consider for simplicity a nonequilibrium n -component isotropic system without polarization and magnetization, the properties of which are continuous

functions of coordinates and time. We formulate the principle of local equilibrium as follows: The particle of a continuum (in the sense of the theory of continuum^{7,8}) is *a priori* characterized by a specific internal energy, u , which is assumed to depend on specific entropy, s , and densities of components, (named weight concentrations in chemistry) $\varrho_1, \varrho_2, \dots, \varrho_n$ of the particle at a given time according to the Gibbs caloric equation

$$u = u(s, \varrho_1, \varrho_2, \dots, \varrho_n). \quad (1)$$

It is assumed for the sake of simplicity that this functional dependence is the same for all particles of the envisaged system, so that the specific internal energy u depends on the particle and time (or place and time) only through the variables s and ϱ_1 through ϱ_n . In such a case, the differential of Eq. (1) need not be restricted to time changes for a given particle but can involve also time changes in a given place and space changes at a given time. All following equations are therefore valid not only for substantial derivatives (time changes for a given particle) but also for partial time derivatives and space gradients (Truesdell and Toupin⁸, Eq. 247.6).

Finally we assume regularity (*cf.*⁸, § 247): All thermodynamic equations can be differentiated as many times as necessary and are always capable of inversion, so that any variable can be expressed as a function of the others.

From Eq. (1) we obtain the differential (*cf.*⁸, § 247)

$$du = T ds + \sum_{i=1}^n r_i d\varrho_i, \quad (2)$$

where the temperature T is defined as

$$T \equiv (\partial u / \partial s)_{\varrho_i}, \quad i = 1 \text{ to } n. \quad (3)$$

The lower index i with the symbol after the parentheses will be understood so that the differentiation is performed at constant $\varrho_1, \varrho_2 \dots, \varrho_n$; analogously in further text. The quantities r_i are defined as

$$r_i \equiv (\partial u / \partial \varrho_i)_{s, \varrho^i}, \quad i = 1 \text{ to } n. \quad (4)$$

The upper index i with the symbol after the parentheses means that the differentiation is performed with respect to ϱ_i while other indexed quantities are constant. Further we introduce the density ϱ of the mixture, the specific volume v and the mass fraction w_i of component i ($i = 1$ to n):

$$\varrho \equiv \sum_{i=1}^n \varrho_i, \quad v \equiv 1/\varrho, \quad w_i \equiv \varrho_i/\varrho. \quad (5), (6), (7)$$

From Eqs (5) and (7) follows (8); further we introduce the specific free energy f :

$$\sum_{i=1}^n w_i = 1; \quad f \equiv u - Ts. \quad (8), (9)$$

Using these equations we define the thermodynamic pressure, P , and the (specific) chemical potential of species i , μ_i :

$$P \equiv \sum_{i=1}^n w_i \varrho^2 r_i; \quad \mu_i \equiv r_i \varrho + f, \quad i = 1 \text{ to } n. \quad (10), (11)$$

Now we shall show that these definitions lead to equations formally agreeing with those obtained from the first formulation of the local equilibrium principle. Afterwards, it will turn out that the agreement is not only formal, since the mentioned quantities and relations in the special case of a homogeneous open system are identical with analogously denoted quantities and relations of classical thermodynamics.

Introducing Eqs (2) and (9) into the differential of internal energy density, ϱu , and expressing $d\varrho$ from (5), rearranging and using the definition (11) we obtain the equation

$$d(\varrho u) = T d(\varrho s) + \sum_{i=1}^n \mu_i d\varrho_i, \quad (12)$$

which is formally identical with that given by Meixner and Reik² and Haase⁵. Expressing the differentials of ϱ_i from Eqs (6) and (7), substituting them in (2) and using the definition of the thermodynamic pressure (10) we obtain

$$du = T ds - P dv + \sum_{i=1}^n r_i \varrho dw_i. \quad (13)$$

Here the quantities w_i are mutually dependent as a result of Eq. (8). Hence,

$$du = T ds - P dv + \sum_{j=1}^{n-1} (r_j \varrho - r_n \varrho) dw_j. \quad (14)$$

With the use of our definition of chemical potential (11), Eq. (14) gives

$$du = T ds - P dv + \sum_{j=1}^{n-1} (\mu_j - \mu_n) dw_j, \quad (15)$$

or Eq. (13) with respect to (8) gives

$$du = T ds - P dv + \sum_{i=1}^n \mu_i dw_i. \quad (16)$$

These results are formally identical with the usual formulation of the Gibbs caloric equation used in irreversible thermodynamics¹⁻⁷.

It should be mentioned that if we start from postulation of a caloric equation in which the specific internal energy u is a function of s, v, w_1 to w_{n-1} (or s, v, w_1 to w_n with the condition (8)), we shall not obtain an unambiguous definition of chemical potential, as stated already by Truesdell (ref.⁸, § 255); instead of Eqs (16) and (15) we shall have

$$du = T ds - P dv + \sum_{i=1}^n {}^T\mu_i dw_i, \quad (17)$$

$$du = T ds - P dv + \sum_{j=1}^{n-1} ({}^T\mu_j - {}^T\mu_n) dw_j, \quad (18)$$

where the chemical potential after Truesdell (ref.⁸, Eq. (255.2)₃), ${}^T\mu_i$, is defined as

$${}^T\mu_i \equiv r_i \varrho + \varphi, \quad i = 1 \text{ to } n. \quad (19)$$

Here φ means an arbitrary function of s, v, w_1 to w_n independent of the index i . This arbitrariness is due to Eq. (8). The quantity ${}^T\mu_i$ is not even in a homogeneous system identical with the chemical potential (ref.⁸, § 260) defined as partial specific free enthalpy; *e.g.*, it does not obey the Gibbs–Duhem equation. This disadvantage is avoided in our theory; the function φ in Eq. (19) is set equal to the specific free energy f and the chemical potential defined by Eq. (11) has, as will be shown in further text, the same properties as partial specific free enthalpy.

Gibbs–Duhem Equation and Partial Specific Quantities

From Eqs (6), (8), (10) and (11) follows an important equation:

$$\sum_{i=1}^n \mu_i w_i = Pv + f. \quad (20)$$

Now, let us define the specific enthalpy h

$$h \equiv u + Pv, \quad (21)$$

and the specific free enthalpy g

$$g \equiv h - Ts = f + Pv = u - Ts + Pv. \quad (22)$$

Eq. (20) can then be rewritten as
$$g = \sum_{i=1}^n \mu_i w_i. \quad (23)$$

On differentiating Eq. (22) and using (15) we obtain

$$dg = -s dT + v dP + \sum_{j=1}^n (\mu_j - \mu_n) dw_j, \quad (24)$$

or using Eq. (16)

$$dg = -s dT + v dP + \sum_{i=1}^n \mu_i dw_i. \quad (25)$$

From Eq. (24) it follows that

$$(\partial g / \partial w_j)_{P,T,w_k} = \mu_j - \mu_n, \quad j = 1 \text{ to } n-1, \quad (26)$$

and with the aid of Eqs (8), (23) and (26) we get

$$\mu_n = g - \sum_{j=1}^{n-1} w_j (\partial g / \partial w_j)_{P,T,w_k}. \quad (27)$$

On differentiating Eq. (23) and comparing the result with (24) or (25), we obtain the Gibbs–Duhem equation

$$-s dT + v dP - \sum_{i=1}^n w_i d\mu_i = 0. \quad (28)$$

This cannot be derived for the Truesdell chemical potentials, Eq. (19), since owing to indeterminacy of the function φ they do not obey Eq. (23).

It is obvious from Eqs (24), (26) and (27) that the chemical potential μ_i , defined by Eq. (11), can be expressed as a function of P , T , w_1 to w_{n-1} . The partial specific quantities can then be defined as follows. Partial specific entropy

$$s_i \equiv -(\partial \mu_i / \partial T)_{P,w_j}, \quad i = 1 \text{ to } n, \quad j = 1 \text{ to } n-1, \quad (29)$$

partial specific volume

$$v_i \equiv (\partial \mu_i / \partial P)_{T,w_j}, \quad i = 1 \text{ to } n, \quad j = 1 \text{ to } n-1. \quad (30)$$

With the aid of the definitions (3), (10), (11), (29) and (30), we can define the partial specific free energy

$$f_i \equiv \mu_i - P v_i, \quad i = 1 \text{ to } n, \quad (31)$$

the partial specific internal energy

$$u_i \equiv \mu_i - P v_i + T s_i = f_i + T s_i, \quad i = 1 \text{ to } n, \quad (32)$$

and the partial specific enthalpy

$$h_i \equiv \mu_i + T s_i = u_i + P v_i, \quad i = 1 \text{ to } n. \quad (33)$$

From Eqs (8), (23), (24) and (29) we obtain

$$s = -(\partial g / \partial T)_{P,w_k} = - \sum_{i=1}^n w_i (\partial \mu_i / \partial T)_{P,w_k} = \sum_{i=1}^n w_i s_i, \quad (34)$$

where $k = 1$ to $n - 1$. Analogously from Eqs (8), (23), (24) and (30)

$$v = (\partial g / \partial P)_{T, w_k} = \sum_{i=1}^n w_i (\partial \mu_i / \partial P)_{T, w_k} = \sum_{i=1}^n w_i v_i. \quad (35)$$

On multiplying Eqs (31)–(33) by w_i , summing from $i = 1$ to n and using Eqs (22), (23), (34) and (35) we obtain analogously

$$f = \sum_{i=1}^n w_i f_i, \quad u = \sum_{i=1}^n w_i u_i, \quad h = \sum_{i=1}^n h_i w_i. \quad (36)–(38)$$

On differentiating Eq. (26) with respect to T or P at constant P or T and w_1 through w_{n-1} and using (24) and (29) or (30) we obtain

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial g}{\partial w_j} \right)_{P, T, w_j} \right)_{P, w_j} = \left(\frac{\partial \mu_j}{\partial T} \right)_{P, w_j} - \left(\frac{\partial \mu_n}{\partial T} \right)_{P, w_j}$$

and analogously $(\partial s / \partial w_j)_{P, T, w_j} = s_j - s_n, \quad j = 1$ to $n - 1,$ (39)

$$(\partial v / \partial w_j)_{P, T, w_j} = v_j - v_n, \quad j = 1$$
 to $n - 1. \quad (40)$

Analogous expressions for the functions f, h and u of the variables P, T, w_1 through w_{n-1} can be derived from Eq. (22) by differentiating with respect to w_j ($j = 1$ to $n - 1$) and using (26), (31)–(33), (39) and (40):

$$(\partial f / \partial w_j)_{P, T, w_j} = f_j - f_n, \quad (\partial h / \partial w_j)_{P, T, w_j} = h_j - h_n, \quad (41), (42)$$

$$(\partial u / \partial w_j)_{P, T, w_j} = u_j - u_n. \quad (43)$$

It is seen that a specific quantity y (*i. e.* f, g, h, s, u or v) is related to the corresponding partial specific quantity y_i by Eqs (23), (26), (34)–(43), which can be written generally as

$$y = \sum_{i=1}^n w_i y_i, \quad (\partial y / \partial w_j)_{P, T, w_j} = y_j - y_n, \quad j = 1$$
 to $n = 1 \quad (44), (45)$

Eqs (8), (44) and (45) give (*cf.* (27))

$$y_n = y - \sum_{j=1}^{n-1} w_j (\partial y / \partial w_j)_{P, T, w_j}, \quad (46)$$

Since y and y_i are also functions of P, T, w_1 through w_{n-1} , it is possible to write (with the use of Eq. (45))

$$dy = (\partial y / \partial T)_{P, w_k} dT + (\partial y / \partial P)_{T, w_k} dP + \sum_{j=1}^{n-1} (y_j - y_n) dw_j \quad (47)$$

with $k = 1$ through $n - 1$. On differentiating Eq. (44), using (8) and comparing

with (47) we obtain the Gibbs–Duhem equation in the general form

$$(\partial y/\partial T)_{P, w_j} dT + (\partial y/\partial P)_{T, w_j} dP - \sum_{i=1}^n w_i dy_i = 0 \quad (48)$$

with $j = 1$ through $n - 1$. (Eq. (28) was derived in an analogous way.)

It should be stressed that these equations were derived regardless of whether the system is homogeneous or not. Equations of the form (48) can therefore be applied to inhomogeneous systems. This is the case, for example, when Eq. (28) is used to derive the Prigogine theorem^{1-7,19} or to prove (for $y = v$, $y_i = v_i$) that a single diffusion coefficient is sufficient to characterize isothermal diffusion in binary mixtures²⁰. Truesdell^{8,15}, however, concluded from the invalidity of Eq. (48) for his quantities ${}^T\mu_i$ (Eq. (19)) that the Gibbs–Duhem equations imply the assumption of homogeneity and hence do not apply for inhomogeneous mixtures. Our method eliminates this objection even when the second formulation of the local equilibrium principle is used.

Homogeneous Systems

The quantities defined on the basis of the postulated Eq. (1) for the general case of an inhomogeneous nonequilibrium system have the same properties as analogously named quantities in an open homogeneous system. It will be shown now that in a special case of a homogeneous system, the quantities defined above are identical with analogously named quantities of classical thermodynamics.

We shall proceed similarly as Truesdell⁸ in § 260. For an open homogeneous system, we shall assume that the specific quantities defined in this work are related to the extensive quantities, namely internal energy U , entropy S and volume V , as follows:

$$U = mu, \quad S = ms, \quad V = mv, \quad (49)-(51)$$

where m denotes mass of the system:

$$m = \sum_{i=1}^n m_i. \quad (52)$$

The masses m_i of the components obey the relation

$$w_i = m_i/m, \quad i = 1 \text{ to } n. \quad (53)$$

Now we shall make use of the function $u = u(s, v, w_1 \dots w_{n-1})$ (Eq. (1) after substituting (6)–(8) which, of course, apply also in this case of a homogeneous equilibrium system) together with Eqs (49)–(53):

$$U = mu(S/m, V/m, m_1/m, \dots, m_{n-1}/m) = U(S, V, m_1, \dots, m_{n-1}, m). \quad (54)$$

Hence, the internal energy U is a function of independent variables $S, V, m_1 \dots m_{n-1}$ and m . Its differential is

$$dU = T dS - P dV + \sum_{j=1}^{n-1} (\mu_j - \mu_n) dm_j + (\partial U / \partial m)_{S, V, m_k} dm, \quad k = 1 \text{ to } n - 1, \quad (55)$$

since according to Eq. (15)

$$(\partial U / \partial S)_{V, m_j, m} = (\partial mu / \partial ms)_{V, m_j, m} = (\partial u / \partial s)_{v, w_j} = T, \quad (56)$$

$$(\partial U / \partial V)_{S, m_j, m} = (\partial mu / \partial mv)_{S, m_j, m} = (\partial u / \partial v)_{s, w_j} = -P, \quad (57)$$

$$(\partial U / \partial m_j)_{S, V, m_j, m} = (\partial mu / \partial m w_j)_{S, V, m_j, m} = (\partial u / \partial w_j)_{s, v, w_j} = \mu_j - \mu_n \quad (58)$$

and $j = 1$ through $n - 1$ in each equation. It is seen that the function U in Eq. (54) is a homogeneous function of first order with respect to all variables S, V, m_1 through m_{n-1} and m , so that according to the Euler theorem

$$U = TS - PV + \sum_{j=1}^{n-1} (\mu_j - \mu_n) m_j + (\partial U / \partial m)_{S, V, m_k} m, \quad k = 1 \text{ to } n - 1. \quad (59)$$

This equation is divided by the total mass of the system m and combined with Eqs (49)–(53) to give

$$u = Ts - Pv + \sum_{j=1}^{n-1} (\mu_j - \mu_n) w_j + (\partial U / \partial m)_{S, V, m_k}, \quad k = 1 \text{ to } n - 1. \quad (60)$$

Here we introduce Eqs (22) and (23) (which, of course, apply also in the special case of a homogeneous system) and obtain

$$\mu_n = (\partial U / \partial m)_{S, V, m_k} = (\partial U / \partial m_n)_{S, V, m_k}, \quad k = 1 \text{ to } n - 1, \quad (61)$$

where the latter equality follows from Eq. (52). Since any component can be regarded as n -th component, the definition (61) of the chemical potential (11) is for a homogeneous system identical with that used in classical thermodynamics.

On introducing Eq. (61) into (55) and expressing dm with the aid of (52) we obtain the classical Gibbs equation

$$dU = T dS - P dV + \sum_{i=1}^n \mu_i dm_i. \quad (62)$$

From this it is apparent that if U, S, V and m_i have the same meaning as in classic thermodynamics, our definitions (3), (10) and (11) of T, P and μ_i and the quantities s, v, u and w_i (Eqs (49)–(53)) are identical with equally named quantities of a homo-

geneous open system. All other quantities can be derived from them by the same relations as in classical thermodynamics, hence they are also identical with equally named quantities of an open homogeneous system.

It should be noted that the Gibbs equation (62) would not hold with Truesdell chemical potentials ${}^T\mu_i$ (Eq. (19)) since they do not obey Eq. (23) used in its derivation. However, it can be written in the specific form with the chemical potentials ${}^T\mu_i$ similarly as with μ_i (Eqs (15)–(18)). This fact forms the basis of Truesdell's criticism of using the Gibbs equation in specific variables in irreversible thermodynamics (ref.⁸, § 255 and 260). The chemical potential μ_i defined in the present work by Eq. (11) fulfils in an inhomogeneous nonequilibrium system the Gibbs caloric equation in the form (15) or (16) and the Gibbs–Duhem equation (28); in a homogeneous system, in which it obtains its classical meaning, it fulfils the Gibbs equation in extensive form (62) (as well as the Gibbs–Duhem equation which can be obtained in extensive form by multiplying Eq. (28) by m and using (50), (51) and (53)).

It can be concluded that the postulation of the caloric equation (1) for a particle of an inhomogeneous continuum (*i.e.* the second formulation of the principle of local equilibrium) ensures, together with suitable definitions, the validity of all usual thermodynamic relations in specific variables in a nonequilibrium continuum, and it is not necessary to use the artificial first formulation of the principle of local equilibrium.

LIST OF SYMBOLS

f	specific free energy
f_i	partial specific free energy
g	specific free enthalpy
h	specific enthalpy
h_i	partial specific enthalpy
m	mass of system
m_i	mass of i -th component
P	thermodynamic pressure
r_i	quantity defined by Eq. (4)
s	specific entropy
s_i	partial specific entropy
S	entropy
T	temperature
u	specific internal energy
u_i	partial specific internal energy
U	internal energy
v	specific volume
v_i	partial specific volume
V	volume
w_i	mass fraction of i -th component
y	specific quantity
y_i	partial specific quantity
μ_i	(specific) chemical potential

- $\bar{\mu}_i$ chemical potential after Truesdell (Eq. (19))
 ρ density of mixture
 ρ_i density of i -th component (weight concentration)
 φ arbitrary function in Eq. (19)

Indexes i, j, k, l denote arbitrary components, index n n -th component.

REFERENCES

1. Prigogine I.: *Etude Thermodynamique des Phénomènes Irréversibles*. Dunod-Desoer, Paris-Liège 1947.
2. Meixner J., Reik H. G. in the book: *Handbuch der Physik* III/2 (S. Flügge, E.). Springer, Berlin 1959.
3. de Groot S. R., Mazur P.: *Nonequilibrium Thermodynamics*. North Holland, Amsterdam 1962.
4. Fitts D. D.: *Nonequilibrium Thermodynamics*. McGraw-Hill, New York 1962.
5. Haase R.: *Thermodynamik der Irreversiblen Prozesse*. Steinkopf, Darmstadt 1964.
6. Prigogine I.: *Introduction à la Thermodynamique des Processus Irréversibles*. Paris 1968.
7. Gyarmati I.: *Nonequilibrium Thermodynamics*. Springer, New York 1970.
8. Truesdell C., Toupin R. in the book: *Handbuch der Physik* III/1 (S. Flügge, Ed.). Springer, Berlin 1960.
9. Meixner J.: *Arch. Rat. Mech. Anal.* 33, 33 (1969).
10. Broer L. J. F. in the book: *Some Basic Properties of Relaxation in Gas Dynamics; Nonequilibrium Flow*, Part II (P. P. Wegener, Ed.). M. Dekker, New York 1970.
11. Meixner J.: *J. Phys. Soc. Japan* 26, Supplement, 212 (1969).
12. Bowen R. M.: *Arch. Rat. Mech. Anal.* 24, 370 (1967).
13. Coleman B. D., Mizel V. J.: *J. Chem. Phys.* 40, 1116 (1964).
14. Nicolis G., Wallenborn J., Velarde M. G.: *Physica* 43, 263 (1969).
15. Truesdell C.: *J. Chem. Phys.* 37, 2336 (1962).
16. Haase R.: *Thermodynamik der Mischphasen*. Springer, Berlin 1956.
17. Samohýl I.: *This Journal* 34, 2483 (1969).
18. Samohýl I.: *This Journal* 34, 2501 (1969).
19. Samohýl I.: *This Journal*, in press.
20. Tyrrell H. J. V.: *Diffusion and Heat Flow in Liquids*. Butterworths, London 1961.

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