

USE OF GIBBS EQUATION IN IRREVERSIBLE THERMODYNAMICS. II.* CALORIC EQUATIONS FOR COMPONENTS AND PARTIAL PRESSURE

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For a nonequilibrium, multicomponent and isotropic continuum, the Gibbs caloric equation for mixtures is expressed with the aid of caloric equations for components and the partial pressure is defined and discussed. Previous definitions of caloric equations for components are shown to be not sufficiently general, while Truesdell's and Bowen's definition of partial pressure is in accord with that in the present work in the special case of caloric equations for components. Even in the general case the total pressure can be expressed as a sum of partial pressures defined in the present work. Bowen's definition of an ideal solution is generally not identical with that in classical thermodynamics.

The principle of local equilibrium of a nonequilibrium continuum was formulated in the preceding communication¹ as a postulation of the Gibbs caloric equation for mixtures in specific variables. This postulate enabled to define the thermodynamic pressure, chemical potential, some other specific quantities of mixtures and partial specific quantities among which the same relations apply as among analogously named quantities in classical thermodynamics (*e.g.* Gibbs–Duhem equations). In the special case of a homogeneous system, these quantities become identical with the classical ones.

In the present work, the Gibbs caloric equation for mixtures is expressed with the aid of caloric equations for components (equations for partial specific internal energies), the partial specific volume is expressed simply in terms of these equations, and the partial pressure is defined.

The thermodynamics of mixtures after Truesdell and Toupin² and Kelly³ is based on postulation of the caloric equations for components in a form which is not the most general one as will be shown below. The partial pressures defined by Truesdell² (in § 255) and Bowen⁴ are for simplified caloric equations for mixtures identical with the definition given in the present work. In contrast to Bowen⁴, we show that even in the general case the total pressure can be expressed as a sum of partial pressures defined in the present work. Bowen's definition⁴ of an ideal solution, however, is not identical with that in classical chemical thermodynamics⁸ (chapter VII in ref.⁵).

Equations in the preceding communication¹ are referred to in further text by their number preceded by I, *e.g.* (I-32).

Caloric Equations for Components and Partial Pressure

We shall express the partial specific internal energies u_i as functions of partial specific entropies, s_1 through s_n , and densities of components, ρ_1 through ρ_n . By dif-

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differentiating the definitoric Eq. (I-32), introducing the differential $d\mu_i$ in variables T, P, w_1 through w_{n-1} and using (I-29) and (I-30) we obtain

$$du_i = T ds_i - P dv_i + \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial w_k} \right)_{T,P,w^k} dw_k, \quad i = 1 \text{ to } n. \quad (1)$$

It is apparent from the definition (I-3), (I-5), (I-7), (I-10) and (I-30) that $v_i = v_i(s, \varrho_1, \dots, \varrho_n)$ and hence

$$dv_i = \left(\frac{\partial v_i}{\partial s} \right)_{\rho_j} ds + \sum_{k=1}^n \left(\frac{\partial v_i}{\partial \varrho_k} \right)_{s,\rho^k} d\varrho_k; \quad i, j = 1 \text{ to } n. \quad (2)$$

Let us assume now that T, P and the derivatives in Eqs (1) and (2) are known. We introduce the differential of Eq. (I-34) into (2) and the result into (1), where we replace the summation by $\sum_{l=1}^n \sum_{j=1}^n (\partial \mu_i / \partial w_j)_{T,P,w^j} \delta_{jl} dw_l$, where the Kronecker symbol δ_{jl} is equal to 1 for $j = l$ and otherwise equal to zero. Thus,

$$du_i = T ds_i - P \left[\left(\frac{\partial v_i}{\partial s} \right)_{\rho_j} \sum_{k=1}^n w_k ds_k + \left(\frac{\partial v_i}{\partial s} \right)_{\rho_j} \sum_{k=1}^n s_k dw_k + \sum_{k=1}^n \left(\frac{\partial v_i}{\partial \varrho_k} \right)_{s,\rho^k} d\varrho_k \right] + \sum_{l=1}^n \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial w_k} \right)_{T,P,w^k} \delta_{kl} dw_l; \quad i, j = 1 \text{ to } n. \quad (3)$$

Eqs (I-5) and (I-7) give by differentiating

$$dw_k = \varrho^{-1} d\varrho_k - \varrho^{-2} \varrho_k \sum_{l=1}^n d\varrho_l; \quad k = 1 \text{ to } n. \quad (4)$$

Eq. (4) introduced into (3) gives after rearrangement

$$du_i = \sum_{k=1}^n \vartheta_{ik} ds_k + \sum_{l=1}^n q_{il} d\varrho_l, \quad i = 1 \text{ to } n, \quad (5)$$

where

$$\vartheta_{ik} \equiv T \delta_{ik} - P \left(\frac{\partial v_i}{\partial s} \right)_{\rho_j} w_k, \quad i, j, k = 1 \text{ to } n, \quad (6)$$

$$q_{il} \equiv P \varrho^{-2} \left(\frac{\partial v_i}{\partial s} \right)_{\rho_j} \sum_{k=1}^n s_k \varrho_k - P \left(\frac{\partial v_i}{\partial s} \right)_{\rho_j} \varrho^{-1} s_l + \varrho^{-1} \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial w_k} \right)_{T,P,w^k} \delta_{kl} - \varrho^{-2} \sum_{k=1}^{n-1} \left(\frac{\partial \mu_i}{\partial w_k} \right)_{T,P,w^k} \varrho_k - P \left(\frac{\partial v_i}{\partial \varrho_l} \right)_{s,\rho^l}; \quad i, j, l = 1 \text{ to } n. \quad (7)$$

The quantities ϑ_{ik} and q_{il} can be hence determined from thermodynamic properties of the mixture.

We now shall express the Gibbs caloric equation for mixtures (I-2) in terms of ϑ_{ik} and q_{i1} (ref.², § 255). Eqs (5) introduced into the differential of Eq. (I-37) give

$$du = \sum_{i=1}^n \sum_{k=1}^n \vartheta_{ik} w_i ds_k + \sum_{i=1}^n \sum_{l=1}^n w_i q_{il} d\varrho_l + \sum_{i=1}^n u_i dw_i. \quad (8)$$

We define

$$q_l \equiv \sum_{i=1}^n w_i q_{il}; \quad l = 1 \text{ to } n. \quad (9)$$

The following expression follows from Eq. (6)

$$\sum_{i=1}^n w_i \vartheta_{ik} = T w_k, \quad k = 1 \text{ to } n, \quad (10)$$

since

$$\sum_{i=1}^n w_i (\partial v_i / \partial s)_{p_j} = 0, \quad j = 1 \text{ to } n, \quad (11)$$

as follows by differentiation of (I-35) with respect to s at constant ϱ_1 through ϱ_n with due account to Eqs (I-5) to (I-7). Introducing Eqs (9) and (10) into (8) we obtain

$$du = T \sum_{k=1}^n w_k ds_k + \sum_{l=1}^n q_l d\varrho_l + \sum_{i=1}^n u_i dw_i. \quad (12)$$

Here we substitute the differential of Eq. (I-34) and use (I-32):

$$du = T ds + \sum_{l=1}^n q_l d\varrho_l + \sum_{i=1}^n f_i dw_i. \quad (13)$$

Now we use Eqs (4) and (I-36) to obtain after rearrangement

$$du = T ds + \sum_{l=1}^n [q_l + \varrho^{-1}(f_l - f)] d\varrho_l, \quad (14)$$

the Gibbs caloric equation for mixtures, (I-2), where the quantities r_i are given by

$$r_i = q_i + \varrho^{-1}(f_i - f), \quad i = 1 \text{ to } n. \quad (15)$$

This in combination with the definition of the thermodynamic pressure P , (I-10), and Eqs (I-7), (I-8), (I-36) gives after rearrangement

$$P = \varrho \sum_{i=1}^n \varrho_i q_i. \quad (16)$$

On introducing Eq. (15) into the definition of chemical potential μ_i (I-11) we obtain

$$\mu_i = \varrho q_i + f_i, \quad i = 1 \text{ to } n. \quad (17)$$

By comparing this with (I-31) we obtain

$$Pv_i = \varrho q_i, \quad i = 1 \text{ to } n, \quad (18)$$

which combined with Eq. (16) gives a simple expression for the partial specific volume v_i :

$$v_i = q_i / \sum_{k=1}^n \varrho_k q_k, \quad i = 1 \text{ to } n. \quad (19)$$

The partial pressure P_i of i -th component can be defined as

$$P_i \equiv \varrho_i v_i P, \quad i = 1 \text{ to } n. \quad (20)$$

With respect to Eqs (I-6), (I-7) and (I-35) it follows that

$$P = \sum_{i=1}^n P_i. \quad (21)$$

That the quantity P_i has the same physical meaning as partial pressure is obvious from the following (ref.², § 215, and⁶). As follows from Eq. (I-35) multiplied by ϱ and combined with (I-6) and (I-7), $\varrho_i v_i$ can be considered as a fraction of volume occupied by the i -th component in a given place at a given time. Hence, $\varrho_i v_i$ can be also considered as a fraction of surface passing through a given place at a given time, occupied by the i -th component. The partial pressure P_i , as defined by Eq. (20), is therefore just that part of the total pressure P which acts only on the i -th component through the considered surface element. It should be noted that in a mixture of ideal gases the term $\varrho_i v_i$ represents molar fraction, and Eqs (20) and (21) express the Dalton law. The partial pressure P_i can be also expressed with the aid of Eqs (16) and (19) as

$$P_i = \varrho \varrho_i q_i, \quad i = 1 \text{ to } n. \quad (22)$$

Comparison with Results of Other Authors and Discussion

For a multicomponent mixture, Truesdell² in § 254 and 255 postulates *a priori* the existence of partial specific quantities and the form of caloric equations for components. Their consequence is the caloric (Gibbs) equation for mixtures.

It can be assumed that our specific quantities¹ of mixtures (y) are identical with those introduced by Truesdell² (the same applies for ϱ and ϱ_i); however, we failed to prove that our partial specific quantities (y_i) are identical with those defined *a priori* by Truesdell². The property $y = \sum_{i=1}^n w_i y_i$, characteristic for both kinds of these partial quantities, is necessary for their identity but not sufficient since the partial

quantities are in both cases generally functions of w_1 through w_{n-1} . A sufficient condition would be the validity of Eqs (I-45) or Gibbs–Duhem equations (I-48), which, however, is not assumed by Truesdell².

For the same reasons, the derivation of partial pressure P_i in ref.⁷, Eqs (85)–(87), is incorrect since in the homogeneous case the intensive quantities are homogeneous functions of zero order with respect to component masses (and not independent of them as assumed⁷).

If we assumed that our partial specific quantities y_i are identical with Truesdell's then the caloric equations for components^{2,3},

$$u_i = u_i(s_i, \varrho_1, \dots, \varrho_n), \quad i = 1 \text{ to } n, \quad (23)$$

are not the most general ones. Indeed, by comparison with our Eqs (5) and (6) it follows that Eq. (23) holds if

$$(\partial v_i / \partial s)_{\rho_j} = 0, \quad i, j = 1 \text{ to } n, \quad (24)$$

and, in accord with Truesdell², § 254,

$$(\partial u_i / \partial s_i)_{\rho_j} = T, \quad i, j = 1 \text{ to } n. \quad (25)$$

According to Eq. (2) v_i is also function of s , v , w_1 through w_{n-1} and, of course, also of T , P , w_1 through w_{n-1} so that

$$\left(\frac{\partial v_i}{\partial s}\right)_{\rho_j} = \left(\frac{\partial v_i}{\partial s}\right)_{v, w_k} = \left(\frac{\partial v_i}{\partial T}\right)_{P, w_k} \left(\frac{\partial T}{\partial s}\right)_{v, w_k} + \left(\frac{\partial v_i}{\partial P}\right)_{T, w_k} \left(\frac{\partial P}{\partial s}\right)_{v, w_k} \quad (26)$$

for $i, j = 1$ to n , $k = 1$ to $n - 1$. On multiplying this by w_1 and adding for $i = 1$ to n we obtain with respect to Eqs (I1), (I-8) and (I-35)

$$\left(\frac{\partial v}{\partial T}\right)_{P, w_k} \left(\frac{\partial T}{\partial s}\right)_{v, w_k} + \left(\frac{\partial v}{\partial P}\right)_{T, w_k} \left(\frac{\partial P}{\partial s}\right)_{v, w_k} = 0, \quad k = 1 \text{ to } n - 1. \quad (27)$$

If we define specific heat at constant volume and composition as

$$c \equiv (\partial u / \partial T)_{v, w_k}, \quad k = 1 \text{ to } n - 1, \quad (28)$$

we can write with respect to Eq. (I-15)

$$(\partial T / \partial s)_{v, w_k} = T / c, \quad k = 1 \text{ to } n - 1. \quad (29)$$

On introducing Eqs (27) and (29) into (26) and rearranging we obtain

$$\left(\frac{\partial v_i}{\partial s}\right)_{\rho_j} = T \left[\left(\frac{\partial v_i}{\partial T}\right)_{P, w_k} \left(\frac{\partial v}{\partial P}\right)_{T, w_k} - \left(\frac{\partial v_i}{\partial P}\right)_{T, w_k} \left(\frac{\partial v}{\partial T}\right)_{P, w_k} \right] / c \left(\frac{\partial v}{\partial P}\right)_{T, w_k} \quad (30)$$

for $i, j = 1$ to $n, k = 1$ to $n - 1$, so that at usual conditions ($c \neq 0, (\partial v/\partial P)_{T, w_k} \neq 0$) Eqs (24) are equivalent to

$$\left(\frac{\partial v_i}{\partial T}\right)_{P, w_k} \left(\frac{\partial v}{\partial P}\right)_{T, w_k} - \left(\frac{\partial v_i}{\partial P}\right)_{T, w_k} \left(\frac{\partial v}{\partial T}\right)_{P, w_k} = 0 \quad (31)$$

for $i = 1$ to $n, k = 1$ to $n - 1$. On subtracting Eqs (31) for j -th and n -th component and using Eq. (I-40) we obtain the condition (31) (hence (24)) in the form

$$\left(\frac{\partial v}{\partial P}\right)_{T, w_j} \left(\frac{\partial^2 v}{\partial T \partial w_j}\right)_{P, w_j} - \left(\frac{\partial v}{\partial T}\right)_{P, w_j} \left(\frac{\partial^2 v}{\partial P \partial w_j}\right)_{T, w_j} = 0 \quad (32)$$

for $j = 1$ to $n - 1$. From this it follows that

$$\begin{aligned} \left[\frac{\partial}{\partial w_j} \left(\frac{\partial P}{\partial T} \right)_{v, w_j} \right]_{T, P, w_j} &= \left\{ \frac{\partial}{\partial w_j} \left[- \left(\frac{\partial v}{\partial T} \right)_{P, w_j} / \left(\frac{\partial v}{\partial P} \right)_{T, w_j} \right] \right\}_{T, P, w_j} = \\ &= - \left(\frac{\partial v}{\partial P} \right)_{T, w_j}^{-2} \left[\left(\frac{\partial v}{\partial P} \right)_{T, w_j} \left(\frac{\partial^2 v}{\partial T \partial w_j} \right)_{P, w_j} - \left(\frac{\partial v}{\partial T} \right)_{P, w_j} \left(\frac{\partial^2 v}{\partial P \partial w_j} \right)_{T, w_j} \right] = 0 \quad (33) \end{aligned}$$

for $j = 1$ to $n - 1$. This means that if Eq. (23) (hence (24)) holds in the general case, the function $(\partial P/\partial T)_{v, w_j}$ must be always independent of composition (at given temperature and pressure), which is certainly not true in general; *e.g.* for a binary mixture the mentioned function should be the same even for its pure components. Hence, Eq. (24) is generally invalid and the caloric equations for components (23) do not represent the general case.

The general caloric equation for a component can have the form $u_i = u_i(s_1, \dots, s_n, \varrho_1, \dots, \varrho_n)$ used for the first time in the present work (Eq. (5)).

We shall compare now our definition of the partial pressure with similar equations derived by Truesdell and Toupin², § 255, for their caloric equations of components (23). From the comparison of Eqs (5), (6) and (9) (with the use of the condition (24)) with equivalent equations in ref.² (Eqs (255.6), (255.9)₁, (255.5); the partial volume is defined differently by (255.5)₁) it follows that Truesdell's Eq. (255.12)₁ is identical with our Eq. (16).

For a still more special case of the caloric equation (ref.², Eq. (255.13))

$$u_i = u_i(s_i, \varrho_i), \quad i = 1 \text{ to } n, \quad (34)$$

our partial pressure P_i is (as follows from Eqs (5), (9) and (22)) given as

$$P_i = \varrho_i \varrho w_i g_{ii} = - [\partial u_i / \partial (1/\varrho_i)]_{s_i}, \quad i = 1 \text{ to } n, \quad (35)$$

so that it is in this special case identical with that defined by Truesdell², Eq. (255.14)₁.

Bowen⁴ attempted in a complicated manner to circumvent the idea of partial pressure and ascertained that in the general case the partial pressure is meaningless. His result for the total pressure in a mixture of fluids (ref.⁴, Eq. (9.13)₂) is in our notation

$$P = -\varrho \sum_{i=1}^n \frac{1}{\varrho_i} \left(\frac{\partial f}{\partial \frac{1}{\varrho_i}} \right)_{T, \rho^i} \quad (36)$$

provided that our total pressure, densities and specific free energy are identical with his quantities (ref.⁴, Eqs (9.11), (9.14), (4.12) and (2.20)). However, we shall show that this equation is equivalent to (21), i.e., that the total pressure P can be expressed as a sum of partial pressures if these are defined by Eq. (20).

The summand in Eq. (36) can be rearranged with the aid of Eq. (I-5) as

$$-\frac{\varrho}{\varrho_i} \left(\frac{\partial f}{\partial \frac{1}{\varrho_i}} \right)_{T, \rho^i} = \varrho_i \varrho \left(\frac{\partial f}{\partial \varrho_i} \right)_{T, \rho^i} = \varrho_i \left[\left(\frac{\partial(\varrho f)}{\partial \varrho_i} \right)_{T, \rho^i} - f \right] \quad (37)$$

for $i = 1$ to n . By the Legendre transformation (I-12) with the aid of the free energy density (obtained by multiplying (I-9) by the density ϱ) we obtain

$$d(\varrho f) = -(\varrho s) dT + \sum_{i=1}^n \mu_i d\varrho_i \quad (38)$$

so that the chemical potential μ_i can be also written as

$$\left[\frac{\partial(\varrho f)}{\partial \varrho_i} \right]_{T, \rho^i} = \mu_i, \quad i = 1 \text{ to } n. \quad (39)$$

Introducing this result into Eq. (37) and using (17) and (22) we obtain

$$-\frac{\varrho}{\varrho_i} \left(\frac{\partial f}{\partial \frac{1}{\varrho_i}} \right)_{T, \rho^i} = P_i + \varrho_i (f_i - f), \quad i = 1 \text{ to } n. \quad (40)$$

If this expression is introduced into Eq. (36) and Eqs (I-5), (I-7) and (I-36) are accounted for, Eq. (21) is indeed the result. Contrary to Bowen⁴, even in the general case in a mixture of fluids the total thermodynamic pressure P can be expressed as a sum of the quantities P_i defined by Eq. (20), to which, as was shown in the discussion of this equation, the physical meaning of partial pressures can be assigned.

For an ideal solution (in a mixture of fluids) defined by Bowen the partial free energy depends, besides temperature, only on the density of the envisaged component (and not on the densities of other components) (ref.⁴, Eq. (8.6)):

$$f_i = f_i(T, \varrho_i), \quad i = 1 \text{ to } n. \quad (41)$$

Eq. (39) with (I-7) and (I-36) gives

$$\mu_i = (\partial \varrho_i f_i / \partial \varrho_i)_T = -\frac{1}{\varrho_i} \left(\partial f_i / \partial \frac{1}{\varrho_i} \right)_T + f_i, \quad i = 1 \text{ to } n, \quad (42)$$

which by comparison with (17) and (22) gives

$$-\left(\partial f_i / \partial \frac{1}{\varrho_i} \right)_T = P_i, \quad i = 1 \text{ to } n. \quad (43)$$

Here the differential quotient is identical with the partial pressure defined for the mentioned ideal solution by Bowen⁴, Eq. (8.11) for mixture of fluids, hence this partial pressure is in our case identical with the quantity P_i defined by Eq. (20). Again, for the same reason as in the discussion of Truesdell's partial quantities at the beginning of this chapter, we assume that also our partial specific quantities u_i , s_i and f_i are identical with the *a priori* defined analogous quantities in ref.⁴, Eqs (2.20), (3.2) and (4.12). Our chemical potential μ_i , Eq. (I-11), is identical with that defined by Bowen⁴ since his Eq. (9.13)₁ is identical with our (39).

Finally, it should be noted that Bowen's definitions of an ideal mixture, Eq. (8.3)⁴ for a mixture of fluids

$$f_i = f_i(T, \varrho_i), \quad s_i = s_i(T, \varrho_i), \quad (44), (45)$$

$$\mu_i = \mu_i(T, \varrho_i), \quad i = 1 \text{ to } n \quad (46)$$

(other definitions (8.3) in ref.⁴ are not important here) are generally not identical with the usual definition of an ideal solution in classical chemical thermodynamics⁸ (ref.⁵, chapter VIII). This definition involves the assumption that the molar chemical potential of component i , $\bar{\mu}_i$, depends at constant T and P only on the molar fraction of i -th component, x_i , so that

$$\mu_i = \bar{\mu}_i(T, P, x_i) / M_i, \quad i = 1 \text{ to } n. \quad (47)$$

Hence (ref.⁵, chapter VII, § 3)

$$s_i = \bar{S}_i(T, P, x_i) / M_i, \quad f_i = \bar{F}_i(T, P, x_i) / M_i \quad (48), (49)$$

for $i = 1$ to n , and the partial molar volume, enthalpy and internal energy are in general independent of composition at constant T and P . (M_i denotes relative molecular mass, \bar{S}_i and \bar{F}_i partial molar entropy and free energy of i -th component.) Further, Eqs (I-6), (I-7) and (I-35) give

$$\varrho_i = x_i M_i / \sum_{k=1}^n x_k \bar{V}_k, \quad i = 1 \text{ to } n, \quad (50)$$

where $\bar{V}_k = M_k v_k$ means partial molar volume of k -th component. It is seen that for a classical ideal mixture characterized by Eq. (47) the values of μ_i , f_i and s_i according to Eqs (47)–(49) remain constant at constant T , P , x_i and changing x_k ($k \neq i$). However, according to Bowen's definitions (44)–(46) these partial quantities can change since ϱ_i according to Eq. (50) is a function of x_1 through x_n which are assumed to change (x_i and $\bar{V}_k = \bar{V}_k(T, P)$ are constant; we assume that \bar{V}_k values are generally not equal and $n > 2$). Hence, the mentioned definitions of an ideal mixture are generally not identical.

The definition of an ideal mixture introduced by Lewis⁸ into chemical thermodynamics is bound to molar quantities. Therefore it cannot be expressed in terms of specific quantities without introducing relative molecular masses.

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LIST OF SYMBOLS

c	spec. heat at const. volume and composition	\bar{V}_k	partial molar volume
\bar{F}_i	partial molar free energy	x_i	molar fraction
M_i	relative molecular mass of i -th component	δ_{ik}	Kronecker symbol
P_i	partial pressure of i -th component	ϑ_{ik}	parameter defined by Eq. (6)
q_i	parameter defined by Eq. (9)	$\bar{\mu}_i$	molar chemical potential
q_{i1}	parameter defined by Eq. (7)	Other symbols are the same as in Part I.	
\bar{s}_i	partial molar entropy		

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