

Entropy of Systems with Internal Variables¹

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Two entropy functions are currently in use: the thermostatic entropy, defined by Carathéodory's theory, and the thermodynamic entropy, defined by the theory of irreversible processes. Both entropy concepts are confined to systems without internal variables, and both can be shown to be equal by substituting the respective balance of internal energy to which they are related by the integrating factor, $1/\theta$. When irreversible internal phenomena are present, represented by internal coordinates and their conjugate affinities, they become part of the entropy production, but not of the energy balance, and the two entropies are no longer equal. It has been shown in the literature that by multiplication by a second integrating factor, an extended entropy function for systems with internal variables can be derived. It is the purpose of this paper to present a method for the determination of this integrating factor. Under certain conditions, the latter may be unity; such is shown to be the case with the Gibbs equation for gas mixtures.

KEY WORDS: entropy; Gibbs equation; internal variables; thermodynamic theory.

1. INTRODUCTION

The present work deals with the entropy of such thermodynamic bodies whose state can be described by an empirical temperature, by a set of deformation coordinates with their conjugate stresses, and by a set of internal coordinates with their conjugate affinities. The latter ones are not forces; therefore, displacements of the internal coordinates do not require work input, and the resulting action does not appear in the balance of internal energy. That, however, makes that action irreversible, which results in a contribution to the entropy production.

¹ Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

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This study is confined to systems which are not history dependent; in that case, the entropy can be calculated within the framework of classical thermostatics, combined with classical nonequilibrium thermodynamics. It has been shown by Edelen [1] that the extension of this entropy concept to systems with internal variables requires the introduction of a second integrating factor; that idea is followed in this paper.

Note that repeated indices always signify summation.

2. THE THERMOSTATIC ENTROPY

The balance equation for the thermostatic part, u' , of the internal energy in the presence of heat input, dq/dt , and work input, dw/dt , into a body of density ρ yields the rate of change of u' as

$$\frac{du'}{dt} = \frac{dq}{dt} + \frac{dw}{dt} \quad (1)$$

where

$$\frac{dq}{dt} = \dot{Q} - \frac{1}{\rho} \operatorname{div} J^q \quad (2)$$

and

$$\frac{dw}{dt} = \frac{d\omega}{dt} + \frac{d\phi}{dt} \quad (3)$$

where Q is the scalar heat source, J^q is the heat flux, ω is the equilibrium work, and ϕ is the viscous work. When the energy balance is written in the form $dB/dt = 0$, the latter becomes

$$\frac{dB}{dt} \equiv \left[\frac{du'}{dt} - \left(\frac{dq}{dt} + \frac{d\omega}{dt} + \frac{d\phi}{dt} \right) \right] = 0 \quad (4)$$

In the limit of a nonviscous adiabatic process, this yields

$$\lim_{\substack{dq/dt \rightarrow 0, \\ d\phi/dt \rightarrow 0}} \left(\frac{dB}{dt} \right) = \frac{du'}{dt} - \frac{d\omega}{dt} = 0 \quad (5)$$

When the equilibrium work can be represented by

$$d\omega = -X_i dx_i \quad (6)$$

and when X_i and u' are given by the constitutive equations of thermostatics,

$$X_i = \hat{X}_i(\Theta, x_1 \cdots x_m) \quad (7)$$

and

$$u' = \hat{u}'(\Theta, x_1 \cdots x_m) \quad (8)$$

where Θ is the empirical temperature, the x_i are the deformation coordinates, and the X_i are the equilibrium stress components, then Eq. (5) becomes

$$\frac{\partial u'}{\partial \Theta} d\Theta + \left(\frac{\partial u'}{\partial x_i} + X_i \right) dx_i = 0 \quad (9)$$

This Pfaffian equation represents the nonviscous adiabatic process, which is associated with the viscous, nonadiabatic energy balance, Eq. (4).

Starting from an initial point $P'(\Theta', x'_1 \cdots x'_m)$, only those displacements of the coordinates correspond to a nonviscous adiabatic process which are compatible with Eq. (9), i.e., only those points P'' are accessible from P' which can be reached by steps $d\Theta, dx_1 \cdots dx_m$ which satisfy Eq. (9). The fact that Eq. (9) was obtained as the limit of a viscous, nonadiabatic process indicates that infinitely close to point P' , there are also points which can be reached only by processes which are either dissipative, nonadiabatic, or both. In other words: infinitely close to P' there are points which are inaccessible by displacements satisfying Eq. (9).

Under these conditions, Carathéodory's inaccessibility principle [2] states that the inexact differential Eq. (9) can be made exact by multiplication by an integrating factor. Thus, the $(\frac{m}{2})$ independent integrability conditions of Eq. (9),

$$\frac{\partial u'}{\partial \Theta} \left(\frac{\partial X_l}{\partial x_k} - \frac{\partial X_k}{\partial x_l} \right) - \left(\frac{\partial u'}{\partial x_k} + X_k \right) \frac{\partial X_l}{\partial \Theta} + \left(\frac{\partial u'}{\partial x_l} + X_l \right) \frac{\partial X_k}{\partial \Theta} = 0 \quad (10)$$

are guaranteed to be satisfied; these conditions now become constraints upon the constitutive Eqs. (7) and (8), which the latter ones have to satisfy in order to be compatible with the laws of thermostatics [3]. Systems whose constitutive equations obey these constraints are called "thermodynamic bodies." Details of the method are given in Ref. 3, where it is also shown that the reciprocal of the integrating factor, called here the "thermostatic temperature," T' , is

$$T' = \Theta \quad (11)$$

Thus, the integration of Eq. (5) yields a surface through P' in the $(\Theta, x_1 \cdots x_m)$ space,

$$s = \int \frac{du' - d\omega}{\Theta} \quad (12)$$

where $s(\Theta, x'_1 \cdots x'_m)$ is the constant of integration, called here “thermostatic entropy.” This entropy concept is defined for equilibrium states only.

A transition between two surfaces of constant thermostatic entropy is given by

$$\Theta \frac{ds}{dt} = \frac{du'}{dt} - \frac{d\omega}{dt} \neq 0 \quad (13)$$

From Eqs. (1) and (3) is obtained

$$\frac{du'}{dt} - \frac{d\omega}{dt} = \frac{dq}{dt} + \frac{d\phi}{dt} \quad (14)$$

Therefore, the laws of thermostatics yield

$$\Theta \frac{ds}{dt} = \frac{dq}{dt} + \frac{d\phi}{dt} \quad (15)$$

i.e., the transition is either nonadiabatic, dissipative, or both. It is reversible only in the case where the heat input is due to a scalar heat source \dot{Q} (Carnot cycle) and where no dissipation occurs. It is assumed in the following that $\dot{Q} = 0$.

3. THE THERMODYNAMIC ENTROPY

A different entropy concept, η , is defined by the entropy balance equation, according to which the rate of entropy increase is equal to the sum of entropy flux, entropy source $\dot{\sigma}$, and entropy production $\dot{\gamma}$; it is called here “thermodynamic entropy”:

$$\rho \frac{d\eta}{dt} = -\text{div } J^s + \dot{\sigma} + \dot{\gamma} \quad (16)$$

where

$$J^s = \frac{J^q}{\Theta} \quad (17)$$

is the preferred approximation for the entropy flux.

In the absence of internal variables, the entropy source is zero, and the entropy production for heat and work input according to Eqs. (2) and (3) is

$$\dot{\gamma}_0 = J^q \cdot \text{grad } \frac{1}{\Theta} + \frac{\rho}{\Theta} \frac{d\phi}{dt} \quad (18)$$

Substituting Eqs. (2), (17), and (18) into Eq. (16) gives

$$\Theta \left(\frac{d\eta}{dt} \right)_0 = \frac{dq}{dt} + \frac{d\phi}{dt} \quad (19)$$

or, from Eq. (14),

$$\Theta \left(\frac{d\eta}{dt} \right)_0 = \frac{du'}{dt} - \frac{d\omega}{dt} \quad (20)$$

Comparing Eqs. (19) and (20) with Eqs. (13) and (15) shows that, in the absence of internal variables, the thermostatic entropy and the thermodynamic entropy are quantitatively equal. However, the definition of η is not restricted to equilibrium states.

4. THE EXTENDED ENTROPY

When the state of a system depends also on internal coordinates ξ_α and their conjugate affinities A_α , then the internal energy u becomes dependent on the ξ_α , such that the constitutive equation is of the form

$$u = \hat{u}(\Theta, x_i; \xi_\alpha) \quad (21)$$

whence

$$du = \frac{\partial u}{\partial \Theta} d\Theta + \frac{\partial u}{\partial x_i} dx_i + \frac{\partial u}{\partial \xi_\alpha} d\xi_\alpha \quad (22)$$

Thus, the change of internal energy of such a system consists of an external energy transfer

$$du' = \frac{\partial u}{\partial \Theta} d\Theta + \frac{\partial u}{\partial x_i} dx_i \quad (23)$$

and of output by an internal energy source

$$du'' = \frac{\partial u}{\partial \xi_\alpha} d\xi_\alpha \quad (24)$$

For such systems, u takes the place of u' in the energy balance Eq. (1), whence in view of Eq. (3),

$$\frac{du}{dt} = \frac{dq}{dt} + \frac{d\omega}{dt} + \frac{d\phi}{dt} \quad (25)$$

The action $A_\alpha(d\xi_\alpha/dt)$ of the internal variables does not enter into the energy balance, but it does enter into the entropy production, which becomes

$$\dot{\gamma} = J^q \cdot \text{grad} \frac{1}{\Theta} + \frac{\rho}{\Theta} \frac{d\phi}{dt} + \rho \frac{A_\alpha}{\Theta} \frac{d\xi_\alpha}{dt} \quad (26)$$

while the energy source appears in the entropy balance as an entropy source,

$$\dot{\sigma} = -\frac{\rho}{\Theta} \frac{du''}{dt}$$

or

$$\dot{\sigma} = -\frac{\rho}{\Theta} \frac{\partial u}{\partial \xi_\alpha} \frac{d\xi_\alpha}{dt} \quad (27)$$

The example of Eq. (67) shows clearly that this term is of the nature of a source.

Substituting Eqs. (26) and (27) into Eq. (16) gives, after algebraic transformation of the divergence term, and substituting Eq. (2) with $\dot{Q} = 0$,

$$\Theta \frac{d\eta}{dt} = \frac{dq}{dt} + \frac{d\phi}{dt} + \left(A_\alpha - \frac{\partial u}{\partial \xi_\alpha} \right) \frac{d\xi_\alpha}{dt}$$

Substituting Eq. (25) gives

$$\Theta \frac{d\eta}{dt} = \frac{du}{dt} - \frac{\partial u}{\partial \xi_\alpha} \frac{d\xi_\alpha}{dt} - \frac{d\omega}{dt} + A_\alpha \frac{d\xi_\alpha}{dt} \quad (28)$$

Substituting Eqs. (22), (23), and (13) gives η as a function of s and ξ_α :

$$\frac{d\eta}{dt} = \frac{ds}{dt} + \frac{A_\alpha}{\Theta} \frac{d\xi_\alpha}{dt} \quad (29)$$

The internal variables, A_α and ξ_α , are not necessarily physically controllable.

In the presence of internal variables, the two entropies, s and η , are no longer equal. Furthermore, while ds is an exact differential, $d\eta$ is not, except in the case where the exactness condition

$$\frac{\partial}{\partial s} \left(\frac{\partial \eta}{\partial \xi_\alpha} \right)_s = \frac{\partial}{\partial \xi_\alpha} \left(\frac{\partial \eta}{\partial s} \right)_{\xi_\alpha} \quad (30)$$

is satisfied. Since $(\partial\eta/\partial s)_{\xi_\alpha} = 1$, this requires, in view of Eq. (29), that in this special case

$$\frac{\partial}{\partial s} \left(\frac{A_\alpha}{\Theta} \right) = 0 \quad (31)$$

i.e., A_α/Θ must be a function of one or more of the ξ_α alone. That important case is discussed in Section 8.

In the case where Eq. (30) is not satisfied, a second integrating factor $N(s, \xi_1 \cdots \xi_n)$ can be found which converts the differential Eq. (29) into an exact differential of the extended entropy, r , for systems with internal variables; the latter is defined as

$$dr = N \left(ds + \frac{A_\alpha}{\Theta} d\xi_\alpha \right) \quad (32)$$

By introducing the “reduced affinity”

$$A'_\alpha = \frac{A_\alpha}{\Theta} \quad (33)$$

Eq. (32) can be written

$$dr = N(ds + A'_\alpha d\xi_\alpha) \quad (34)$$

5. THE INTEGRATING FACTOR

The Pfaffian differential equation associated with Eq. (34) is

$$ds + A'_\alpha d\xi_\alpha = 0 \quad (35)$$

where ds is given by Eq. (15). When at a given point P' all displacements $d\xi_\alpha$ are chosen, then Eq. (35) determines ds , which by virtue of Eq. (15), determines $dq + d\phi$. Thus, only such irreversible processes are admissible where the sum $dq + d\phi$ satisfies Eq. (35). Any other process would lead to points in the s, ξ_α space which are inaccessible from P' by means of Eq. (35). Therefore, the inaccessibility principle is applicable, the integrability conditions are satisfied, and the integrating factor N exists.

The irreversible process Eq. (35) can now be represented in the $(n+1)$ -dimensional $(s, \xi_1 \cdots \xi_n)$ space.

When there is a single internal coordinate, the extended entropy is given by Eq. (34) as the exact differential equation

$$dr = N(ds + A' d\xi) \quad (36)$$

with the exactness condition

$$\frac{\partial}{\partial s} \left(\frac{\partial r}{\partial \xi} \right) = \frac{\partial}{\partial \xi} \left(\frac{\partial r}{\partial s} \right)$$

or

$$A' \left(\frac{\partial N}{\partial s} \right)_{\xi} + N \left(\frac{\partial A'}{\partial s} \right)_{\xi} = \left(\frac{\partial N}{\partial \xi} \right)_s \quad (37)$$

with the boundary condition

$$\text{for } \xi = \text{const: } N = 1, \quad \left(\frac{\partial N}{\partial s} \right)_{\xi} = 0 \quad (38)$$

Therefore, the differential equation for N is

$$N \left(\frac{\partial A'}{\partial s} \right)_{\xi} = \left(\frac{\partial N}{\partial \xi} \right)_s \quad (39)$$

The integral is

$$N = \varphi(s) e^{\int \partial A' / \partial s \, d\xi} \quad (40)$$

From the boundary condition Eq. (38) follows $\varphi(s) = 1$. Therefore,

$$N = e^{\int \partial A' / \partial s \, d\xi} \quad (41)$$

and

$$dr = e^{\int \partial A' / \partial s \, d\xi} (ds + A' d\xi) \quad (42)$$

When n pairs of internal variables A'_α , ξ_α are given, the total differential of $\ln N$ is, on account of Eq. (38),

$$d(\ln N) = \frac{\partial \ln N}{\partial \xi_1} d\xi_1 + \frac{\partial \ln N}{\partial \xi_2} d\xi_2 + \dots$$

or, from Eq. (39),

$$d(\ln N) = \frac{\partial A'_1}{\partial s} d\xi_1 + \frac{\partial A'_2}{\partial s} d\xi_2 + \dots$$

Integration gives the integrating factor as

$$N = e^{\int \partial A'_\alpha / \partial s \, d\xi_\alpha} \quad (43)$$

where the constant of integration is taken as 1, according to the boundary condition Eq. (38). Equation (43) is to be substituted into Eq. (34).

6. THE CONSTRAINTS ON THE CONSTITUTIVE EQUATION FOR THE AFFINITIES

Since the inaccessibility principle guarantees that the integrability conditions of Eq. (35) are satisfied, these conditions must be considered as constraints on the constitutive equations for the affinities A'_α in the $(s, \xi_1 \cdots \xi_n)$ space where

$$A'_\alpha = \hat{A}'_\alpha(s, \xi_1 \cdots \xi_n) \quad (44)$$

With α in Eq. (35) having values from 1 to n , there are $\binom{n}{2}$ independent integrability conditions. These are

$$\left(\frac{\partial A'_k}{\partial \xi_l} - \frac{\partial A'_l}{\partial \xi_k} \right) + \left(A'_k \frac{\partial A'_l}{\partial s} - A'_l \frac{\partial A'_k}{\partial s} \right) = 0 \quad (45)$$

According to Eq. (15), the processes which cause a change in s are independent of those which bring about a change in the internal coordinates. Thus, the derivatives of A' with respect to ξ are independent of those with respect to s , and each of the two parentheses in Eq. (45) must be taken as zero independently.

This results in the following equations:

$$A'_l \frac{\partial A'_k}{\partial s} = A'_k \frac{\partial A'_l}{\partial s} \quad (46)$$

or

$$\frac{\partial \ln A'_k}{\partial s} = \frac{\partial \ln A'_l}{\partial s} \quad (47)$$

and

$$\frac{\partial A'_k}{\partial \xi_l} = \frac{\partial A'_l}{\partial \xi_k} \quad (48)$$

Equation (47) shows that the derivatives with respect to s must be equal to a common function E for every k or l , i.e., for every α there is

$$\frac{\partial \ln A'_\alpha}{\partial s} = E(s, \xi_1 \cdots \xi_n) \quad (49)$$

The function E must be determined for each system individually. Equations (48) and (49) are the constraints to which the constitutive Eqs. (44) are subjected. Only those functions \hat{A}'_α are thermodynamically admissible which comply with these constraints.

The differential of Eq. (34) must be exact for all affinities A'_α compatible with the constraints given by Eqs. (48) and (49). It is now shown that Eq. (34) combined with Eq. (43) does indeed satisfy both the n exactness conditions containing the derivatives with respect to s ,

$$\frac{\partial}{\partial \xi'_\alpha} \left(\frac{\partial r}{\partial s} \right) = \frac{\partial}{\partial s} \left(\frac{\partial r}{\partial \xi'_\alpha} \right) \quad (50)$$

and the $\binom{n}{2}$ exactness conditions without derivatives with respect to s ,

$$\frac{\partial}{\partial \xi'_k} \left(\frac{\partial r}{\partial \xi'_l} \right) = \frac{\partial}{\partial \xi'_l} \left(\frac{\partial r}{\partial \xi'_k} \right) \quad (51)$$

In view of Eqs. (34) and (38), Eq. (50) can be written

$$\frac{\partial N}{\partial \xi'_\alpha} = N \frac{\partial A'_\alpha}{\partial s} \quad (52)$$

These n conditions are satisfied by Eq. (43) for any function A'_α .

In view of Eq. (34), Eq. (51) can be written

$$N \left(\frac{\partial A'_l}{\partial \xi'_k} - \frac{\partial A'_k}{\partial \xi'_l} \right) = A'_k \frac{\partial N}{\partial \xi'_l} - A'_l \frac{\partial N}{\partial \xi'_k} \quad (53)$$

According to Eq. (48), the left side is zero; therefore,

$$A'_k \frac{\partial N}{\partial \xi'_l} = A'_l \frac{\partial N}{\partial \xi'_k}$$

Substituting Eq. (52) gives

$$A'_k \frac{\partial A'_l}{\partial s} = A'_l \frac{\partial A'_k}{\partial s} \quad (54)$$

These $\binom{n}{2}$ conditions are satisfied by Eq. (46). Therefore, for systems with internal variables, the entropy concept must be extended by including the second integrating factor, N .

The constraints given by Eqs. (48) and (49) restrict the constitutive equations for the affinities to types whose derivatives possess a certain symmetry. Considering that $A_\alpha d\xi'_\alpha$ represents energy, A_α must include the factor $R\theta$, where R is the gas constant. The simplest example for such a constitutive equation is, in terms of A'_α ,

$$A'_\alpha = Rf'(\xi'_\alpha) \{ 1 + \beta g(s) [f(\xi'_1) + \cdots + f(\xi'_\alpha) + \cdots + f(\xi'_n)] \} \quad (55)$$

where $f(\xi_\alpha)$ and $g(s)$ are dimensionless functions, defined by the system in question. The factor β is an empirical constant. Differentiation according to Eq.(49) yields

$$\frac{\partial \ln A'_\alpha}{\partial s} = \frac{\beta g'(s)[f(\xi_1) + \dots + f(\xi_\alpha) + \dots + f(\xi_n)]}{1 + \beta g(s)[f(\xi_1) + \dots + f(\xi_\alpha) + \dots + f(\xi_n)]} \quad (56)$$

which satisfies the constraint given by Eq. (49). The differentiations of Eq. (55) with regard to the internal coordinates yields

$$\frac{\partial A'_k}{\partial \xi_l} = \beta R g(s) f'(\xi_k) f'(\xi_l) = \frac{\partial A'_l}{\partial \xi_k} \quad (57)$$

which satisfies the constraint given by Eq. (48).

For the example of Eq. (55) it can now be verified that the derivations of A'_α with respect to s are, as stipulated in the discussion of Eq. (45), indeed not solely dependent on the derivatives with respect to ξ . Combining Eqs. (55), (56), and (57) yields the following relation between the terms occurring in the integrability condition given by Eq. (45):

$$A'_l \frac{\partial A'_k}{\partial s} = \frac{\partial A'_k}{\partial \xi_l} \frac{R g'(s)}{\beta g^2(s)} \frac{A'_k}{R f'(\xi_k)} \left(\frac{A'_k}{R f'(\xi_k)} - 1 \right) \quad (58)$$

7. THE FREE ENERGY

For a system with internal variables, a “thermodynamic temperature” is defined as

$$T = \frac{\Theta}{N} \quad (59)$$

with N given by Eq. (43). Then, a function ψ can be defined which has all the properties of a “free energy” [1]:

$$\psi(T, x_i, \xi_\alpha) = u' - Tr \quad (60)$$

with r given by the differential Eq. (32). From Eqs. (60), (13), (6), (59), and (32) follows

$$d\psi = -r dT - X_i dx_i - A_\alpha d\xi_\alpha \quad (61)$$

whence

$$\frac{\partial \psi}{\partial T} = -r; \quad \frac{\partial \psi}{\partial x_i} = -X_i; \quad \frac{\partial \psi}{\partial \xi_\alpha} = -A_\alpha \quad (62)$$

Further,

$$\frac{\partial}{\partial T} \left(\frac{\partial \psi}{\partial \xi_\alpha} \right)_{x,T} = - \frac{\partial A_\alpha}{\partial T}$$

and from Eq. (32),

$$\frac{\partial}{\partial \xi_\alpha} \left(\frac{\partial \psi}{\partial T} \right)_{x,\xi} = - \left(\frac{\partial r}{\partial \xi_\alpha} \right)_{x,T} = - \frac{A_\alpha}{T}$$

Since Eq. (61) is an exact differential, it follows that

$$\left(\frac{\partial A_\alpha}{\partial T} \right)_{x,\xi} = \frac{A_\alpha}{T} \quad (63)$$

8. GAS MIXTURES

An example for a system with internal variables is a gas mixture, where the composition changes irreversibly through diffusion or chemical reaction. Since neither of these processes requires work input, the mole ratios v_k correspond to the internal coordinates ξ_α , and the mixing entropies correspond to the reduced affinities A'_α . In such a mixture, the internal variables are controllable.

The internal energy per mole of mixture is

$$u = v_k u_k(\Theta, v) \quad (64)$$

where

$$v_k \equiv \xi_\alpha \quad (65)$$

i.e., u_k takes the place of u' in Eq. (23), and Eq. (6) becomes the work of compression,

$$d\omega = -p dv$$

where p is the pressure and v is the volume of 1 mol mixture. The dependence of the internal energy on the internal coordinates is, from Eq. (64),

$$\left(\frac{\partial u}{\partial v_k} \right)_{\Theta, v} = u_k \quad (66)$$

The entropy source becomes, according to Eqs. (27), (65), and (66),

$$\dot{\sigma} = - \frac{\rho}{\Theta} u_k \frac{dv_k}{dt} \quad (67)$$

In the above notation, Eq. (28) becomes

$$\Theta \frac{d\eta}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - (u_k - A_k) \frac{dv_k}{dt} \quad (68)$$

The chemical potential is defined as [4]

$$\mu_k = \left(\frac{\partial u}{\partial v_k} \right)_{\eta, v}$$

It can be seen from Eq. (68) that

$$\left(\frac{\partial u}{\partial v_k} \right)_{\eta, v} = u_k - A_k$$

Therefore,

$$\mu_k = u_k - A_k$$

and Eq. (68) becomes the ‘‘Gibbs equation’’ for gas mixtures,

$$\Theta \frac{d\eta}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \mu_k \frac{dv_k}{dt} \quad (69)$$

Differentiating Eq. (64) and substituting into Eq. (68) gives

$$\Theta \frac{d\eta}{dt} = v_k \frac{du_k}{dt} + p \frac{dv}{dt} + A_k \frac{dv_k}{dt} \quad (70)$$

From classical thermodynamics it follows [4] that $\int A_k dv_k$ is the mixing entropy multiplied by Θ :

$$A_k = \Theta \left(\frac{\partial \eta}{\partial v_k} \right)_{\Theta, v} = -R\Theta(1 + \ln v_k) \quad (71)$$

This is a special case of Eq. (55) where $\beta = 0$, and $f'(\xi_\alpha) = -(1 + \ln \xi_\alpha)$.

The reduced affinity for gas mixtures now becomes

$$A'_\alpha = -R(1 + \ln v_k) \quad (72)$$

where

$$\xi_\alpha \equiv v_k$$

Therefore, in this special case where A'_α is a function of ξ_α alone, there is

$$\frac{\partial A'_\alpha}{\partial S} = 0$$

and from Eq. (43),

$$N = 1$$

i.e., $d\eta$ in Eqs. (69) and (70) is already an exact differential, and no second integrating factor is needed. This is an example of the case mentioned in Eq. (31).

The function E in Eq. (49) can now be calculated for a gas mixture where $\beta = 0$. In that case, Eq. (56) gives the trivial result

$$E = 0 \tag{73}$$

Since, for gas mixtures, A'_α depends only on its conjugate ξ_α , the constraint given by Eq. (48) yields the trivial identity $0 = 0$.

ACKNOWLEDGMENT

The author gratefully acknowledges the numerous stimulating discussions which he had during the preparation of this work with his colleague Professor Charles Speziale of Stevens Institute of Technology.

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