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New formulation of local-equilibrium thermodynamics

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ABSTRACT
This study points out that the conventional separation of balance equations for energy in fluids into a flow and a source term is not thermodynamically valid. It corrects this inadequacy and thereby identifies an expression for the nonnegative rate of entropy production that is a sum of products of kinetic and thermodynamic quantities. Here, the kinetic and corresponding thermodynamic quantities are the flow of internal energy and the gradient of the reciprocal temperature; the flow of each component and the negative gradient of its chemical potential divided by the temperature; the rate of each chemical reaction and its affinity divided by the temperature; and the conversion of mechanical energy into internal energy and the reciprocal temperature. One of the deductions from this expression is that the internal energy of a fluid never turns into its mechanical energy on its own, a fact which had heretofore not been actually proved in general. On the other hand, the stability condition of local equilibrium leads to a nonpositive integral over the volume of a system under suitable boundary conditions. The integrand is found to be the same form as the entropy production expression, with each thermodynamic quantity replaced by its time derivative. It thus turns out that the thermodynamic quantities always vary temporally so as to lower the entropy production of the system. It can also be seen that if a particular kinetic and thermodynamic quantity pair alone is considered only locally, then the absolute value of the latter invariably lessens with time.

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I. INTRODUCTION
Thermodynamics describes how systems of matter change their physical states. It was originally concerned with changes between equilibrium states. It is nowadays extended so as to include nonequilibrium situations.

Many such treatments are based on the so-called assumption of local equilibrium. It states that even if equilibrium is not reached in a system as a whole, thermodynamic variables can be defined for each infinitesimally small (but microscopically large) element of the system and that they satisfy the same thermodynamic relations as in equilibrium systems. The resulting local-equilibrium thermodynamics has successfully been applied to various phenomena in physics, chemistry, biology, and engineering.

(In passing, other nonequilibrium thermodynamic theories have also been actively pursued that are free from the local equilibrium hypothesis. For their review and recent developments, Refs. 4 and 5 may be consulted.)

On the other hand, it seems that the fundamental aspects of local-equilibrium thermodynamics are not fully appreciated. This is partly because balance equations for energy in fluids had hitherto not been treated properly. In this article, we rectify this situation and investigate what this thermodynamics can really predict.

The remainder of the paper is organized as follows. In Sec. II, we first derive from the Gibbs relation at a fixed position and balance equations for internal energy and matter an expression for the (rate of) entropy production, which is different in form from, but equivalent to the well-known expression. To ascertain whether the present form has any significance, the energy balance equation employed is examined from a thermodynamic viewpoint in Sec. III. As a result, we find that earlier treatments do not appropriately separate the balance equation for internal energy into a flow term and a source term,
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the latter representing the transformation of kinetic and potential energy into internal energy. We present the correct way of separation. It is thereby understood in Sec. IV that the expression for the entropy production obtained in Sec. II is formed by a sum of products of kinetic and thermodynamic quantities, with the former including the corrected flow and source term for the internal energy. The implications of this result are discussed. In Sec. V, to gain insight into the temporal behavior of the thermodynamic quantities, we also consider the stability condition of local equilibrium, which finally yields an inequality that involves the time derivatives of the thermodynamic quantities multiplied by their corresponding kinetic ones. On the basis of this inequality and the entropy production expression, we clarify how the thermodynamic quantities vary with time under the influence of the kinetic ones. Section VI compares our approach with previous ones in local-equilibrium thermodynamics. Section VII gives a brief summary of this work. As to the internal energy, there is another definition that is regarded as more precise (for multicomponent systems) than the customary one used in the main part of this article. The theory developed there is modified according to this definition in Appendix D.

II. ENTROPY PRODUCTION

We consider a fluid system comprised of $n$ components among which $r$ chemical reactions take place and derive an expression for the (rate of) entropy production on the basis of local equilibrium. We start with the Gibbs relation as applied to the time variation of local state variables at a fixed point in the system:6

$$
T \frac{\partial (ps)}{\partial t} = \frac{\partial (pu)}{\partial t} - \sum_{i=1}^{n} \mu_i \frac{\partial \rho_i}{\partial t},
$$

(1)

where $t$ is the time; $T$ the absolute temperature; $s$ and $u$ the specific entropy and specific internal energy, respectively; $\rho_i$ and $\mu_i$ the partial density and specific chemical potential, respectively, of component $i$; and $\rho$ the total density,

$$
\rho = \sum_{i=1}^{n} \rho_i.
$$

(2)

The Gibbs relation is different in form from that employed more commonly to deduce an entropy production expression [which is Eq. (24) below]. Appendix A shows that they are both valid in local-equilibrium thermodynamics. The rate of change of the partial density and of the internal energy density are given by the familiar balance equations,$^{7,8}$

$$
\frac{\partial \rho_i}{\partial t} = -\nabla \cdot (\rho_i \mathbf{v}_i) + \sum_{j=1}^{r} \nu_{ij} M_i w_j,
$$

(3)

$$
\frac{\partial (pu)}{\partial t} = -\nabla \cdot (J_i + \rho_i \mathbf{v}) - \mathbf{P} \cdot \nabla \mathbf{v} + \sum_{i=1}^{r} \mathbf{F}_i,
$$

(4)

where $\mathbf{v}_i$ and $M_i$ are the velocity and molar mass, respectively, of component $i$; $\mathbf{v}$ the velocity of the center of mass,

$$
\mathbf{v} = \sum_{i=1}^{r} \rho_i \mathbf{v}_i / \rho;
$$

(5)

$J_i$ the diffusion flow of component $i$ relative to the center of mass,

$$
J_i = \rho_i (\mathbf{v}_i - \mathbf{v});
$$

(6)

and $\mathbf{F}_i$ a force per unit mass acting on component $i$. The quantity $w_j$ is the rate of chemical reaction $\gamma$ expressed in moles per unit time and unit volume, and $\nu_{ij}$ is the stoichiometric coefficient of component $i$ in reaction $\gamma$, taken as positive or negative depending on whether it is a net product or reactant, respectively, in the reaction. The quantity $J_i$ is the heat flow and $\mathbf{P}$ is the stress (or pressure) tensor. Insertion of Eqs. (3) and (4) into Eq. (1) yields

$$
\frac{\partial (ps)}{\partial t} = \frac{1}{T} \left[ -\nabla \cdot (J_i + \rho_i \mathbf{v}) - \mathbf{P} \cdot \nabla \mathbf{v} + \sum_{i=1}^{r} \mathbf{F}_i \right] + \sum_{i=1}^{n} \mu_i \nabla \cdot (\rho_i \mathbf{v}_i) + \sum_{j=1}^{r} w_j A_j,
$$

(7)

where $A_j$ is the chemical affinity of reaction $\gamma$,

$$
A_j = -\sum_{i=1}^{n} \nu_{ij} M_i \mu_i.
$$

(8)

To split the right-hand side of Eq. (7) into the divergence of the flow of entropy and its source i.e., the entropy production, we need to specify the former. To this end, we consider the time change of the entropy density in terms of those of the temperature, pressure, and composition

$$
\frac{\partial (ps)}{\partial t} = \left[ \frac{\partial (ps)}{\partial T} \right]_{P, \{\rho_i\}} \frac{\partial T}{\partial t} + \left[ \frac{\partial (ps)}{\partial \rho_p} \right]_{T, \{\rho_i\}} \frac{\partial \rho_p}{\partial t} + \sum_{i=1}^{n} \left[ \frac{\partial (ps)}{\partial \rho_i} \right]_{T, \{\rho_p, \rho_i\}} \frac{\partial \rho_i}{\partial t}
$$

$$
= \frac{\rho_p}{T} \frac{\partial T}{\partial t} - \alpha \frac{\partial \rho_p}{\partial t} + \sum_{i=1}^{n} \beta_i \frac{\partial \rho_i}{\partial t},
$$

(9)

where $p$ is the pressure; the subscripts $\{\rho_i\}$ and $\{\rho_p\}$ signify that every partial density and every partial density except $\rho_i$ are held constant, respectively; $\rho_p$ is the specific heat at constant pressure; $\alpha$ the expansion coefficient at constant pressure,

$$
\alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_{P, \{\rho_i\}},
$$

(10)

with $v = 1/\rho$ the specific volume; and $s_i$ the partial specific entropy of component $i$. In Eq. (9), the quantity $\rho_p c_p \partial T/\partial t$ represents a time change in enthalpy per unit volume at constant pressure and composition. If, therefore, it is separated into a flow term and a source term, then the former should include $-\nabla \cdot \mathbf{q}$. Here, if $\mathbf{q}$ contains a flow of enthalpy due to transport of matter, it should be removed from $\mathbf{q}$. The heat flow $\mathbf{q}$ in question is defined from the total energy flow $\mathbf{J}_e$ as

$$
\mathbf{J}_e = \rho \mathbf{v} \mathbf{e} + \mathbf{P} \cdot \mathbf{v} + \sum_i \phi_i \mathbf{J}_i + \mathbf{J}_q,
$$

(11)

where $\phi_i$ is the potential energy corresponding to the force $\mathbf{F}_i$,

$$
\mathbf{F}_i = -\nabla \phi_i,
$$

(12)

and $e$ is the total specific energy,

$$
e = \frac{1}{2} \mathbf{v}^2 + \phi + u,
$$

(13)

with $\phi$ the total specific potential energy,

$$
\phi = \sum \rho_i \phi_i / \rho.
$$

(14)
We assume that the stress tensor $\mathbf{P}$ can be decomposed into the scalar hydrostatic pressure $p$ and the viscous stress tensor $\Pi$:

$$\mathbf{P} = p \mathbf{I} + \Pi,$$  \hspace{1cm} (15)

where $\mathbf{I}$ is the unit tensor. It then follows from Eqs. (11), (13), and (15) that

$$J_c = \rho \left( \frac{1}{2} \nabla^2 + \phi \right) v + \rho hv + \Pi \cdot v + \sum_i \phi_i J_i + J_q,$$  \hspace{1cm} (16)

where $h$ is the specific enthalpy, i.e., the enthalpy flow due to diffusion, where

$$\rho h = \sum_i \rho_i h_i$$

have been used. The quantity $\rho_i \partial T_i / \partial t$ thus contains the flow $J_q = \sum_i h_i J_i$, which may be regarded as the heat flow attributed to pure conduction. The first term in the last member of Eq. (9) then yields the term

$$\frac{1}{T} \nabla \cdot \left( J_q - \sum_i h_i J_i \right) = - \nabla \cdot \left( \frac{\rho - \sum_i h_i J_i}{T} \right) \nabla \left( \frac{1}{T} \right)$$

and hence the entropy flow due to pure heat conduction, $(J_q - \sum_i h_i J_i) / T$. In view of Eq. (3), the last term of Eq. (9) gives the term

$$- s_i \nabla \cdot (\rho_i v_i) = - \nabla \cdot (s_i \rho_i v_i) + \rho_i v_i \cdot \nabla s_i,$$

and hence the entropy flow due to transport of matter, $\sum_i s_i \rho_i v_i$. Consequently, the total entropy flow $J_s$ becomes

$$J_s = \frac{J_q - \sum_i h_i J_i}{T} + \sum_i s_i \rho_i v_i = \frac{J_q + \rho hv - \sum_i \mu_i \rho_i v_i}{T},$$  \hspace{1cm} (20)

where use has been made of Eq. (18) and the relation

$$\mu_i = h_i - T s_i.$$  \hspace{1cm} (21)

With Eqs. (15), (17), and (20), Eq. (7) can be rewritten as

$$\frac{\partial \rho s}{\partial t} = - \nabla \cdot \left( \frac{J_q + \rho hv - \sum_i \mu_i \rho_i v_i}{T} \right) + \frac{1}{T} \nabla \cdot \left( \nabla P - \Pi : \nabla v + \sum_i J_i \cdot F_i \right) - \sum_i \rho_i v_i \cdot \nabla \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum_i w_i A_v$$

$$= - \nabla \cdot J_c + \sigma,$$  \hspace{1cm} (22)

where $\sigma$ is the entropy production given by

$$\sigma = \left( J_q + \rho hv \right) \cdot \nabla \left( \frac{1}{T} \right) + \frac{1}{T} \left( v \cdot \nabla p - \Pi : \nabla v + \sum_i J_i \cdot F_i \right)$$

$$- \sum_i \rho_i v_i \cdot \nabla \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum_i w_i A_v.$$  \hspace{1cm} (23)

This is the desired result. (It has already been obtained in a different manner and used in a different context from here.) Equation (23) may appear different from the more frequently cited expression

$$\sigma = J_q \cdot \nabla \left( \frac{1}{T} \right) - \frac{1}{T} \Pi : \nabla v + \frac{1}{T} \sum_i J_i \cdot F_i - \sum_i \nabla \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum w_i A_v,$$  \hspace{1cm} (24)

That Eqs. (23) and (24) are actually equivalent can be readily seen with the aid of the Gibbs–Duhem relation as applied to the gradients of local variables, as

$$\rho h \nabla \left( \frac{1}{T} \right) + \frac{1}{T} \nabla p - \sum_i \rho_i \nabla \left( \frac{\mu_i}{T} \right) = 0$$  \hspace{1cm} (25)

[which also comes from Eqs. (A7) and (A9) in Appendix A]. We reproduce Eq. (24) by forming the scalar product of Eq. (25) and the velocity $v$, subtracting the result from Eq. (23), and noting Eq. (6).

Some readers might wonder whether the foregoing analysis leading to Eq. (23) is necessary because reversing the procedure just stated, one may gain it simply from the known results (24) and (25). With the latter equations alone, however, we would not be able to determine a priori how to combine them to arrive at a meaningful expression for the entropy production, since there are an infinite number of such combinations that are equivalent to Eq. (24). We thus need to show in the first place that Eq. (23) is also a natural consequence of the Gibbs relation, as is Eq. (24).

When local equilibrium is assumed, it is usual to hypothesize also that the second law of thermodynamics holds true locally. This means that the (local) entropy production is nonnegative:

$$\sigma \geq 0,$$  \hspace{1cm} (26)

where the equality pertains only to equilibrium processes, which are not considered hereafter.

[It may be added that local equilibrium does not necessarily warrant the validity of the second law. The inequality (26) as such can be violated for systems with delayed response, for instance. See, e.g., Ref. 10.]

III. ENERGY BALANCE EQUATIONS

Local-equilibrium treatments normally adopt Eq. (24) when they need an expression for the entropy production. To explore the possible utility of Eq. (23), we now turn our attention to the energy balance Eq. (4) that is one of the requisites for its derivation. This equation implies that the flow of internal energy is $J_q + \rho hv$ and its source is $- P_1 \nabla v + \sum_i J_i \cdot F_i$, which describes the conversion of kinetic and potential energy into internal energy. This result is obtained without going into thermodynamic detail. The true internal energy flow should, however, be determined in accordance with local-equilibrium thermodynamics. We draw on the Gibbs relation to this aim. Since the entropy flow is given by Eq. (20), the left
hand-side of Eq. (1) contains the flow $J_u + p\rho v = \sum_i \mu_i \rho_i \nu_i$, while the last term $\sum_i \mu_i \partial p_i / \partial t$ has the flow $\sum_i \mu_i \rho_i \nu_i$. Equation (1) therefore requires that the internal energy flow $J_u$ be

$$J_u = J_q + p\rho v,$$

(27)

instead of $J_q + \rho \nu v$. [Another derivation of Eq. (27) is given in Appendix B.] The physical meaning of $J_u$ becomes clearer when it is written in another form:

$$J_u = \sum_i \rho_i u_i + \left( J_q - \sum_i h_i \right) + p \sum_i \rho_i \nu_i,$$

(28)

where we have used Eqs. (18) and (27) and the relation

$$h_i = u_i + p \nu_i,$$

(29)

with $\nu_i$ the partial specific volume of component $i$. The three terms on the right of Eq. (28) denote, respectively, the flow of internal energy due to transport of matter, the pure heat flow, and the mechanical work performed by the pressure on a moving volume. In classical (equilibrium) thermodynamics, the so-called pressure-volume work causes a change in internal energy of a closed system. The last term in Eq. (28) therefore constitutes a natural extension of this work to flow systems. Equation (27) converts the original balance Eq. (4) into

$$\frac{\partial (\rho u)}{\partial t} = -\nabla \cdot \left( J_t + p \rho v \right) + \nu \cdot \nabla p - \Pi : \nabla v + \sum_i J_i \cdot F_i,$$

(30)

$$= -\nabla \cdot J_u + \Phi,$$

where $\Phi$ is the interconversion of energy given by

$$\Phi = \nu \cdot \nabla p - \Pi : \nabla v + \sum_i J_i \cdot F_i,$$

(31)

Although the accustomed balance Eq. (4) is valid in itself, it would be preferable for its correct interpretation to write it in the form (30).

The foregoing consideration also affects understanding of the conventional balance equation for kinetic and potential energy, which reads

$$\frac{\partial}{\partial t} \left[ \rho \left( \frac{1}{2} v^2 + \phi \right) \right] = -\nabla \cdot \left[ \rho \left( \frac{1}{2} v^2 + \phi \right) v + \rho v \cdot \nabla \phi + \sum_i \nu_i J_i \right]$$

$$+ P : \nabla v - \sum_i J_i \cdot F_i,$$

(32)

with the quantity preceded by the divergence operator being the flow of kinetic and potential energy and the rest its source. The corresponding balance Eq. (4) is deduced by subtracting Eq. (32) from the law of conservation of total energy expressed as

$$\frac{\partial (\rho e)}{\partial t} = -\nabla \cdot J_e,$$

(33)

and using Eqs. (11) and (13). Subtraction of Eq. (30) from Eq. (33) hence leads to the corrected version of the balance equation for kinetic and potential energy:

$$\frac{\partial}{\partial t} \left[ \rho \left( \frac{1}{2} v^2 + \phi \right) \right] = -\nabla \cdot \left[ \rho \left( \frac{1}{2} v^2 + \phi \right) v + \Pi : \nabla v + \sum_i \nu_i J_i \right]$$

$$- \nu \cdot \nabla p + \Pi : \nabla v - \sum_i J_i \cdot F_i.$$  

(34)

It is to be noted from Eqs. (27), (32), and (34) that the mechanical work $p v$ is here included in the internal energy flow $J_u$ and excluded from the flow of kinetic (and potential) energy.

It has thus far been tacitly assumed that the potential $\phi_i$ is time-independent. If it depends on time, then the term $\sum_i \mu_i \partial \phi_i / \partial t$ needs to be added to the right-hand sides of Eqs. (32)–(34).

### IV. RECONSIDERATION OF ENTROPY PRODUCTION

We are now ready to examine in detail our expression (23) for the entropy production. It is first seen that it comprises the internal energy flow $J_u$, the energy conversion $\Phi$ introduced in Eqs. (27) and (31), respectively. With the inequality (26), Eq. (23) can be written as

$$\sigma = J_u \cdot \nabla \left( \frac{1}{T} \right) + \Phi \cdot \nabla \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \left( \sum_i \nu_i A_i \right) > 0.$$

(35)

This equation shows that the entropy production consists of four kinds of contributions representing different nonequilibrium processes. The four terms in the second member are related, respectively, to the flow of internal energy, the transformation of kinetic and potential energy into internal energy, the flow of matter (in the presence of gradients of thermodynamic variables), and chemical reactions. Each term may be regarded as the product of a kinetic and a thermodynamic quantity. The kinetic quantity is either the internal energy flow $J_u$, the energy conversion $\Phi$, the flow of each component $\rho_i \nu_i$, or each chemical reaction rate $w_i$. The corresponding thermodynamic quantity is $\nabla (1/T)$, $1/T$, $-\nabla (\mu_i/T)$, or $A_i/T$, respectively.

To clarify what the inequality (35) implies, we consider special situations where one process connected to each term exists on its own or prevails over other processes. It then follows that

$$J_u \cdot \nabla \left( \frac{1}{T} \right) > 0,$$

(36)

$$\Phi > 0,$$

(37)

$$\rho_i \nu_i \cdot \nabla \left( \frac{\mu_i}{T} \right) < 0,$$

(38)

or

$$w_i \frac{A_i}{T} > 0.$$

(39)

[Some readers might wonder whether the separate use of the terms $J_u \cdot \nabla (1/T)$, $\Phi/T$, and $\rho_i \nu_i \cdot \nabla (\mu_i/T)$ in the inequalities (36)–(38) violates the Galilean invariance of the entropy production because these terms are in general not Galilean invariant. That this is not the case is explained in Appendix C.]

The inequalities (36) and (38) state that the flows of internal energy and each component occur in the direction of decreasing temperature and $\mu_i/T$, respectively. The inequality (39) indicates that a chemical reaction proceeds in the direction that corresponds to positive affinity.

The inequality (37) means that $\Phi > 0$, i.e., the kinetic and potential energy is always transformed into the internal energy and the reverse process never happens, as long as other phenomena are
absent or negligible. Such a fact may be widely believed to be true, but it seems that it had not been actually proved thermodynamically before. The inequality (37) may represent its first general proof based on the second law of thermodynamics. By way of illustration, imagine a simple situation where one stirs a fluid vigorously and adds kinetic energy to it. Due to friction, this energy then turns into thermal energy. The opposite never occurs. It may be surprising that in the literature, no one appears to have ever explained even this basic (and pedagogical) case rigorously in light of thermodynamics. The inequality (37) may serve to elucidate such a phenomenon. Another simple example is a process known as Joule (or Ohmic) heating. When an electric current is passed through an electrolyte solution, the resulting electrical (or potential) energy is irreversibly converted to heat. The inequality (37) also covers this case, although as far as the irreversible conversion of potential energy into internal energy is concerned, its proof may be viewed as already given elsewhere. (Further details concerning applications of this inequality will be reported in a later paper.)

V. STABILITY CONDITION FOR LOCAL EQUILIBRIUM

In the preceding section, we have relied on the positivity of the entropy production, which is postulated by the second law of thermodynamics. This law also imposes conditions for local-equilibrium states to be stable. Those conditions are expressed in various forms.

We now study what the inequality (40) results in from the perspective of the individual terms in the present analysis. Substitution of Eqs. (3) and (30) into it gives

$$\frac{\partial}{\partial t} \left( \frac{1}{T} \right) \nabla \cdot \mathbf{J}_{u} + \frac{\partial}{\partial t} \left( \frac{1}{T} \right) \Phi + \sum_{i} \frac{\partial}{\partial t} \left( \frac{\mu_{i}}{T} \right) \nabla \cdot (\rho \mathbf{v}_{i}) + \sum_{i} \frac{\partial}{\partial t} \left( \frac{A_{i}}{T} \right) w_{i} < 0, \quad (41)$$

To make this compatible with the relation (35), we integrate the left side over the volume $V$ of a system and apply Gauss’s divergence theorem, obtaining

$$- \int_{\Omega} \frac{\partial}{\partial t} \left( \frac{1}{T} \right) \mathbf{J}_{u} \cdot d\mathbf{A} + \int_{\partial \Omega} \sum_{i} \frac{\partial}{\partial t} \left( \frac{\mu_{i}}{T} \right) \rho \mathbf{v}_{i} \cdot d\mathbf{A} + \int_{V} \left( \mathbf{J}_{u} \cdot \frac{\partial}{\partial t} \left( \frac{1}{T} \right) \nabla \left( \frac{\mu_{i}}{T} \right) \right) \nabla \cdot (\rho \mathbf{v}_{i}) + \int_{V} \left( \sum_{i} w_{i} \frac{\partial}{\partial t} \left( \frac{A_{i}}{T} \right) \right) dV < 0, \quad (42)$$

where $\Omega$ is the surface enclosing the system and $d\mathbf{A} = n d\Omega$, with $n$ the unit normal vector directed outwardly from a surface area $d\Omega$. To eliminate the surface integrals, we introduce boundary conditions that stipulate either that the temperature and chemical potentials be independent of time on the surface, i.e., the surface be in a stationary state or that the flows of heat and matter through the surface disappear. The expression (42) thus reduces to

$$\int \left( \mathbf{J}_{u} \cdot \frac{\partial}{\partial t} \left( \frac{1}{T} \right) \nabla \left( \frac{\mu_{i}}{T} \right) \right) \nabla \cdot (\rho \mathbf{v}_{i}) + \sum_{i} w_{i} \frac{\partial}{\partial t} \left( \frac{A_{i}}{T} \right) dV < 0. \quad (43)$$

We notice here that the same kinetic and thermodynamic quantities appear in the same form as in the relation (35), except that the thermodynamic quantities are now preceded by time derivative signs. The expressions (35) and (43) show that the thermodynamic quantities always change in such a way that the entropy production of the entire system decreases.

To understand the implications of the individual terms in the inequality (43), we consider specific circumstances again where nonequilibrium process alone is present at only one point in the system and the other processes are absent or negligible over the whole range [or at least at that point in cases in which the process present is either the energy conversion $\Phi$ or a chemical reaction, in consideration of the local expression (41)]. We then have at the point

$$\mathbf{J}_{u} \cdot \frac{\partial}{\partial t} \left( \frac{1}{T} \right) \nabla \left( \frac{\mu_{i}}{T} \right) < 0, \quad (44)$$

$$\Phi \frac{\partial}{\partial t} \left( \frac{1}{T} \right) < 0, \quad (45)$$

$$\rho \mathbf{v}_{i} \cdot \frac{\partial}{\partial t} \left( \frac{1}{T} \right) \nabla \left( \frac{\mu_{i}}{T} \right) > 0, \quad (46)$$

$$w_{i} \frac{\partial}{\partial t} \left( \frac{A_{i}}{T} \right) < 0. \quad (47)$$

Combination of the inequalities (44)–(47) with (36)–(39), respectively, leads to the following reasonable consequences: The flows of internal energy and each component lessen the gradients of temperature and its chemical potential times the reciprocal temperature, respectively; the transformation of kinetic and potential energy into internal energy causes a rise in temperature; and the progress of a chemical reaction decreases its affinity divided by the temperature.

VI. COMPARISON WITH PRIOR WORK

The present treatment differs from customary ones in several respects. Comparison between them may be in order.

This theory regards the flow $\mathbf{J}_{u}$ and the source term $\Phi$ in the internal energy balance as given by Eqs. (27) and (31), whereas they used to be taken as

$$\mathbf{J}_{u} = \Phi + \rho \mathbf{v}, \quad (48)$$

$$\Phi = -P \nabla \mathbf{v} + \sum_{i} \mathbf{J}_{i} \cdot \mathbf{F}_{i}. \quad (49)$$

We have shown in Sec. III that $\mathbf{J}_{u}$ and $\Phi$ are in accord with local-equilibrium thermodynamics, but that $\mathbf{J}_{u}$ and $\Phi$ are not. There is another drawback to $\Phi'$; it is about its sign. As described in Sec. IV,
as far as the energy conversion represented by $\Phi$ is predominant over other phenomena, it is invariably positive. We now illustrate that this is not necessarily the case with $\Phi'$. For simplicity, we examine a uniform one–component fluid where an arbitrary velocity field is assigned. In this situation, the energy conversion is generally the only process that occurs initially, and Eqs. (23) [or (24)], (31), and (49) become

$$\sigma = -\frac{1}{T} \Pi \cdot \nabla \mathbf{v} > 0,$$

(50)

$$\Phi = -\Pi \cdot \nabla v,$$

(51)

$$\Phi' = -P \cdot \nabla v = -\rho \nabla v - \Pi \cdot \nabla v.$$

(52)

By virtue of the inequality (50), $\Phi$ is always positive. The quantity $\Phi'$, however, does not have a definite sign. Although it happens to be positive especially for incompressible fluids where $\nabla \cdot \mathbf{v} = 0$, it can be negative in principle for other (compressible) fluids. This denotes that the internal energy can be spontaneously transformed into the kinetic energy, which may be contradictory to our physical intuition.

Incidentally, the term $\nabla \cdot \mathbf{v}$ in Eq. (31), which is characteristic of our theory, vanishes in the above example. In general, this term indicates that when a fluid moves in the direction of increasing (decreasing) pressure, the kinetic (internal) energy turns into the internal (kinetic) energy. Detection of such an effect experimentally or by means of molecular dynamics may serve to verify the validity of local-equilibrium thermodynamics.

In this work, we have considered the entropy production as a sum of products of kinetic and thermodynamic quantities. On the other hand, conventional treatments view it as a sum of products of flows and thermodynamic forces. Some flows and thermodynamic forces coincide with our kinetic and thermodynamic quantities, respectively. Introduction of flows and forces thereby is useful in describing nonequilibrium phenomena in some cases, e.g., in systems that are close to (overall) equilibrium, where the flows are represented as linear combinations of the forces. In general, however, there is no firm thermodynamic basis for how to define such flows and forces in the entropy production. Furthermore, their physical meanings become unclear in some circumstances, particularly when the stability condition for local equilibrium is incorporated.

A simple case in point is provided. Let us take up a uniform multicomponent system and imagine that each component is subjected to a uniform external force and has a uniform velocity as a consequence. Equation (23) [or (24)] and the inequality (41) then yield

$$\sigma = \frac{1}{T} \sum_i J_i \cdot F_i > 0,$$

(53)

$$\frac{\partial}{\partial t} \left( \frac{1}{T} \right) \sum_i J_i \cdot F_i < 0.$$ (54)

In this instance, $J_i$ and $F_i/T$ are usually taken as the flow and thermodynamic force, respectively. It follows from the inequalities (53) and (54) that the temperature rises at each point. As described in Section V, this is due to the conversion of the potential energies into the internal energy (i.e., $\Phi = \sum J_i \cdot F_i$). Alternatively, the temperature may be held fixed with the aid of a suitable thermostat, since the equality sign can be restored to the inequality (54) in accordance with the relation (40), in which case a stationary state is realized. If the external forces are time-independent, therefore, the quantity $F_i/T$ either changes temporally in a nonstationary state or remains constant in a stationary state. In the former case, the term force may not be appropriate for $F_i/T$ since it has an undesirable (or unnatural) dependence on the temperature. Some researchers might still argue that the definition of the force is merely a matter of expediency. In either event, adoption of the force does not lead, by itself, to the fact of the temperature rise, which may be best explained in terms of the energy conversion.

Lastly, we compare the inequality (43) with evolution criteria for nonequilibrium systems developed by Glansdorff and Prigogine, who have put forward three versions of them. They are based on the same stability condition (40) and boundary conditions as the inequality (43). They are similar in form to the latter, although they are depicted in terms of forces and velocities in contrast to the kinetic and thermodynamic quantities used in the latter. One of the evolution criteria is in general derived without approximation, but is limited to systems without convection. This criterion includes as a special case Prigogine’s theorem of minimum entropy production, which is thought to be valid only close to equilibrium owing to approximations involved. The criterion is then extended to another one, which takes convective effects into consideration, but which assumes systems to be in a mechanical steady state. The third criterion removes this assumption, and employs a certain flow and some forces that have no clear physical meaning [containing the total external force $F = \sum \rho_i F_i/\rho$ and the center of mass velocity $\mathbf{v}$, respectively]. The inequality (43), on the other hand, relies solely on the stability condition (40) and the boundary conditions imposed and contains definite kinetic and thermodynamic quantities. It may be expected to apply not only to linear systems near equilibrium but also to nonlinear systems far from equilibrium, as long as local equilibrium is maintained.

VII. CONCLUSIONS

In this article, we have treated the balance equation for internal energy correctly and have thereby shown that the local entropy production of a system can be expressed as

$$\sigma = \sum_a P_a X_a > 0,$$

(55)

where $P_a$ and $X_a$ are a kinetic and a thermodynamic quantity, respectively. The notation $P_a X_a$ stands for either the product of two scalars or the scalar product of two vectors. From the stability of local equilibrium, we have obtained an integral over the volume of the system under appropriate boundary conditions:

$$\int \sum_a \frac{\partial X_a}{\partial t} dV < 0.$$ (56)

It follows from the relations (55) and (56) that the thermodynamic quantities generally vary with time in a way so that the entropy production for the whole system is reduced. More specifically, if a particular term $P_a X_a$ in the inequality (55) and the corresponding term $P_a X_a/\partial t$ in the inequality (56) alone exist only locally, then...
the thermodynamic quantity $X_a$ invariably relaxes in absolute value with time.

**APPENDIX A: VARIOUS FORMS OF GIBBS RELATION**

In local-equilibrium thermodynamics, it is normally assumed that the spatial variations of thermodynamic quantities in a nonequilibrium system are not too large and their temporal variations are slow compared to the relaxation of microscopic processes in the system. As a result, the gradients of thermodynamic quantities at a fixed time and their time variations at a fixed location are supposed to obey the same forms of thermodynamic relations as at equilibrium. It hence follows that the same types of relations also hold for a mass element of the system moving with its center of mass.

Thus, the Gibbs relation (based on specific quantities), valid at equilibrium, i.e.,

$$T\delta s = \delta u + p\delta v - \sum_i \mu_i \delta x_i,$$

with $\delta$ an infinitesimal variation, $p$ the pressure, $v = 1/\rho$ the specific volume, and $x_i = \rho_i/\rho$ the mass fraction of component $i$, implies that

$$T\delta s = \nabla^T \delta u + p\nabla^T \delta v - \sum_i \mu_i \nabla x_i,$$  \hspace{1cm} (A2)

$$T\frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} + p\frac{\partial v}{\partial t} - \sum_i \mu_i \frac{\partial x_i}{\partial t},$$  \hspace{1cm} (A3)

and hence

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{dv}{dt} - \sum_i \mu_i \frac{dx_i}{dt},$$  \hspace{1cm} (A4)

where $d/dt$ designates the so-called substantial time derivative, i.e., the time rate of change as one moves with the local center of mass. It is related to the time derivative at a fixed position by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla,$$  \hspace{1cm} (A5)

where $\mathbf{v}$ is the center of mass velocity [defined by Eq. (5)].

On the other hand, the thermodynamic relation defining the specific Gibbs free energy $g$ is

$$g = u + pv - Ts,$$  \hspace{1cm} (A6)

which, upon noting that $g = \sum_i \mu_i x_i$, becomes

$$\sum_i \mu_i x_i = u + pv - Ts.$$  \hspace{1cm} (A7)

By virtue of this expression, Eq. (A1) may be rewritten as

$$T\delta (ps) = \delta (pu) - \sum_i \mu_i \delta p_i,$$  \hspace{1cm} (A8)

which is the Gibbs relation on a per unit volume basis. This then yields

$$T\nabla (ps) = \nabla (pu) - \sum_i \mu_i \nabla p_i,$$  \hspace{1cm} (A9)

$$T\frac{\partial (ps)}{\partial t} = \frac{\partial (pu)}{\partial t} - \sum_i \mu_i \frac{\partial p_i}{\partial t},$$  \hspace{1cm} (A10)

and hence

$$T\frac{d(ps)}{dt} = \frac{d(pu)}{dt} - \sum_i \mu_i \frac{dp_i}{dt}.$$  \hspace{1cm} (A11)

Equation (A10) is given in Ref. 6 and is adopted as Eq. (1) in this paper, whereas we often see the Gibbs relation in the form (A4) in the literature. They are both applicable as well as the other expressions (A2), (A3), (A9), and (A11) in local-equilibrium thermodynamics.

**APPENDIX B: ALTERNATIVE PROOF OF EQ. (27)**

This equation can also be derived from the thermodynamic relation defining the specific Gibbs free energy $g$ [i.e., Eq. (A6)], which, when multiplied by the density $\rho$, becomes

$$\rho g = \rho u + p - T \rho s.$$  \hspace{1cm} (B1)

Differentiating Eq. (B1) with respect to time, we have

$$\frac{\partial (\rho u)}{\partial t} = \frac{\partial (T \rho s)}{\partial t} - \frac{\partial p}{\partial t} + \frac{\partial (\rho g)}{\partial t}.$$  \hspace{1cm} (B2)

In view of Eqs. (20) and (22), the first and third terms on the right yield the flows $\mathbf{J}_u = \rho \mathbf{v} - \sum \mu_i \mathbf{v}_i$ and $\sum \mu_i \mathbf{v}_i$, respectively. The left-hand side hence has the flow given by Eq. (27).

**APPENDIX C: GALILEAN INVARIANCE OF ENTROPY PRODUCTION**

To ensure that the entropy production is always nonnegative irrespective of the frame of reference, one may postulate its Galilean invariance, i.e., that the entropy production is the same in all inertial frames. It is indeed seen that each term in the usual entropy production (24) is Galilean invariant and hence so is the entropy production. In Eq. (35), on the other hand, the first three terms are generally not Galilean invariant, but the entropy production as a whole, being equivalent to Eq. (24), is Galilean invariant. It should be noticed that since one cannot require each term in the entropy production to be invariably nonnegative, these terms do not need to be Galilean invariant separately; it is sufficient that the entire entropy production is Galilean invariant.

When the terms in the inequalities (36)–(38) are each present

$$\mathbf{J}_u \cdot \nabla \left( \frac{1}{T} \right) = \mathbf{J}_q \cdot \nabla \left( \frac{1}{T} \right) = \sigma \text{ for } \{ \mathbf{v}_i \} = \{ 0 \}, \{ w_\gamma \} = \{ 0 \},$$  \hspace{1cm} (C1)

$$\Phi \frac{1}{T} \left( - \Pi : \nabla \mathbf{v} + \sum_i \mathbf{J}_i \cdot \mathbf{F}_i \right) = \sigma$$  \hspace{1cm} (C2)

for $\nabla T = \nabla p = \{ \nabla \mu_i \} = \{ 0 \}, \{ w_\gamma \} = \{ 0 \}$,

$$\rho \mathbf{v}_i \cdot \nabla \left( \frac{\mu_i}{T} \right) = \frac{1}{T} \cdot \nabla \mu_i = \sigma$$  \hspace{1cm} (C3)

with the notation $\{ \mathbf{v}_i \}$ etc. referring to every $\mathbf{v}_i$ etc. They thus make themselves and hence the entropy production $\sigma$ Galilean
invariant. Except for these cases, they are Galilean variant. This is also true when one of them dominates the entropy production (35). For instance, when

$$J_u \cdot \nabla \left( \frac{1}{T} \right) > \frac{\Phi}{T} + \sum \rho_i \mathbf{v}_i \cdot \nabla \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum \omega A_i,$$

one may still have

$$J_u \cdot \nabla \left( \frac{1}{T} \right) > 0,$$

which case is included in the inequality (36). Although the term \( \rho_i \mathbf{v}_i \cdot \nabla (1/T) \) contained in \( J_u \cdot \nabla (1/T) \) is Galilean variant, it cancels out [according to the Gibbs–Duhamel relation (25)] those parts of the terms \( \Phi/T \) and \(- \sum \rho_i \mathbf{v}_i \cdot \nabla (\mu_i/T) \) [neglected in the inequality (C5)] that are also Galilean variant, making the whole entropy production Galilean invariant. The other inequalities (37) and (38) should also be understood in a similar way.

**APPENDIX D: TREATMENT BASED ON A DIFFERENT DEFINITION OF INTERNAL ENERGY**

For multicomponent systems, the internal energy can be defined differently from the text, which adopts the conventional definition. In this Appendix, we describe how this alternative definition affects the expressions deduced there.

The specific internal energy \( u \) employed above is defined by Eq. (13), namely,

$$u = c - \phi - \frac{1}{2} \mathbf{v}^2.$$

Another specific internal energy \( u^* \) has been proposed by de Groot and Mazur:

$$u^* = c - \phi - \frac{1}{2} \sum x_i \mathbf{v}_i^2,$$

where \( x_i \) is the mass fraction of component \( i \),

$$x_i = \rho_i/\rho.$$

The quantity \( u^* \) may be worthier of the name internal energy than the usual \( u \) because the macroscopic kinetic energies of all components are completely excluded from the former. It follows from Eqs. (2), (5), and (D1)–(D3) that the two internal energies are related by

$$u^* = u - \frac{1}{2} \sum x_i \mathbf{v}_i \cdot (\mathbf{v}_i - \mathbf{v})^2.$$

In accordance with Eq. (D2), the total energy flow may be represented as, instead of Eq. (11),

$$J_u = \sum \rho_i \mathbf{v}_i \mathbf{v}_i^* + \rho \mathbf{v}^2 + \mathbf{P} \cdot \mathbf{v} + \sum \phi_i J_i,$$

which defines the corresponding heat flow \( J_q^* \). Comparison of Eqs. (11) and (D5), along with Eqs. (13) and (D4), gives the relationship between \( J_q^* \) and \( J_q \):

$$J_q^* = J_q - \frac{1}{2} \sum x_i \mathbf{v}_i^2.$$

To obtain a balance equation for \( u^* \), we multiply both sides of Eq. (D4) by \( \rho \), differentiate them with respect to time, and use Eqs. (17), (30), (D4), and (D6) and the specific enthalpy \( h^* \) defined from \( u^* \),

$$h^* = u^* + \rho \mathbf{v},$$

with the result that

$$\frac{\partial (\rho u^*)}{\partial t} = -\mathbf{v} \cdot \left( J_q + \rho \mathbf{v}^2 + \mathbf{P} \cdot \mathbf{v} + \sum \phi_i J_i \right)$$

$$- \frac{1}{2} \sum \rho_i \mathbf{v}_i \cdot (\mathbf{v}_i - \mathbf{v})^2,$$

where use has also been made, for simplicity, of an identity \( \gamma \) for an arbitrary local variable \( a \),

$$\rho \frac{\partial a}{\partial t} = \frac{\partial (\rho a)}{\partial t} + \mathbf{v} \cdot (\rho \mathbf{v}),$$

with \( \partial/dt \) the substantial derivative [as given by Eq. (A5)]. Equation (D8) corresponds to Eq. (30) and provides expressions for the internal energy flow \( J_q^* \) and the interconversion of energy \( \Phi^* \):

$$J_u^* = J_q^* + \rho h^* \mathbf{v},$$

$$\Phi^* = \mathbf{v} \cdot \nabla p - \nabla \mathbf{v} + \sum J_i \cdot F_i - \frac{1}{2} \sum \nabla \cdot (\mathbf{v}_i J_i),$$

$$- \frac{\rho}{2} \sum \frac{d[x_i (\mathbf{v}_i - \mathbf{v})^2]}{dt},$$

In the present context, the Gibbs relation should read

$$\frac{\partial (\rho^*)}{\partial t} = \frac{\partial (\rho u^*)}{\partial t} - \sum \mu_i^* \frac{\partial \rho_i}{\partial t},$$

where \( s^* \) and \( \mu_i^* \) are the specific entropy and specific chemical potential of component \( i \), respectively, each deriving from \( u^* \). Inserting Eqs. (3) and (D8) into Eq. (D12) and proceeding as in the text, we have a balance equation for entropy

$$\frac{\partial (\rho s^*)}{\partial t} = -\mathbf{v} \cdot \left( J_q + \rho h^* \mathbf{v} - \sum \mu_i^* \rho_i \mathbf{v}_i \right) + \left( J_q^* + \rho h^* \mathbf{v} \right) \cdot \nabla \left( \frac{1}{T} \right)$$

$$+ \frac{1}{T} \mathbf{v} \cdot \nabla p - \nabla \mathbf{v} + \sum J_i \cdot F_i - \frac{1}{2} \sum \nabla \cdot (\mathbf{v}_i J_i),$$

$$- \frac{\rho}{2} \sum \frac{d[x_i (\mathbf{v}_i - \mathbf{v})^2]}{dt} - \sum \rho_i \mathbf{v}_i \cdot \nabla \left( \frac{\mu_i^*}{T} \right) + \frac{1}{T} \sum \omega A_i,$$

where \( A_i^* \) is the affinity defined by

$$A_i^* = -\sum \omega A_i \mu_i^*,$$

as in Eq. (8). Equation (D13), together with Eqs. (D10) and (D11), yields an expression for the entropy production \( \sigma^* \) based on \( u^* \):
\[ \sigma^* = J_u^* \cdot \nabla \left( \frac{1}{T} \right) + \Phi^* \cdot \nabla \left( \frac{\mu^*}{T} \right) + \frac{1}{T} \sum_y w_y A_y^* > 0, \quad (D15) \]

which is to be compared with the expression (35).

The stability condition (40) for local equilibrium should be replaced here by

\[ \frac{\partial}{\partial t} \left( \frac{1}{T} \right) \frac{\partial (\rho u^*)}{\partial t} - \sum_i \frac{\partial}{\partial t} \left( \mu_i^* \right) \frac{\partial \rho_i}{\partial t} \leq 0. \quad (D16) \]

If Eqs. (3) and (D8) are substituted into this relation, it follows from the same procedure as that in the text that

\[ \int \left[ \left( J_u^* \cdot \nabla \left( \frac{1}{T} \right) + \Phi^* \cdot \nabla \left( \frac{\mu^*}{T} \right) + \frac{1}{T} \sum_i \rho_i v_i \cdot \nabla \left( \mu_i^* \right) \right) + \sum_y w_y \frac{\partial (A_y^*)}{\partial t} \right] dV < 0, \quad (D17) \]

in place of the inequality (43).

The results (D15) and (D17) may be discussed in the same manner as the relations (35) and (43) were done before.

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