ABSTRACT: The conversion of mechanical (i.e., kinetic and potential) energy into internal (or thermal) energy is ubiquitous in fluids, while the reverse process seems less common. Little is known a priori about in what circumstances the former conversion occurs or not. The present study investigates this problem by applying thermodynamics to nonequilibrium situations. It is thereby found that if a fluid is uniform in temperature, pressure, and composition, then its mechanical energy necessarily turns into its internal energy but not vice versa (with its kinetic energy determined relative to the vessel holding it). This result is essentially based on the second law of thermodynamics, but the conventional way of evaluating the energy conversion needs to be corrected to obtain it. It may constitute the first thermodynamically general and rigorous explanation of why heat is usually generated, e.g., when a liquid is stirred vigorously or when an electric current flows through an electrolyte solution. If a fluid is not uniform, however, it is possible that its internal energy is transformed into its mechanical energy. Such behavior is illustrated by considering a representative case in which two identical pure fluids are brought into contact with each other at the same temperature but at different pressures.

1. INTRODUCTION

Energy conversion is an important subject of research in physical sciences from both theoretical and practical perspectives. Energy conversion between different materials (as in heat engines) has been actively studied thermodynamically (for such recent work, see, e.g., refs 1 and 2). Energy can also convert inside the same substance. Famous natural phenomena involving such processes are ocean circulation (and related phenomena)3 and the occurrence of tropical cyclones (such as hurricanes),6 to name but a few. In laboratories, more common cases may be the generation of heat from kinetic or potential energy in fluids. For instance, when a fluid (especially a liquid) is agitated using a stirrer, its temperature generally increases. This is due to the fact that the stirrer gives it kinetic energy, which then dissipates as heat owing to fluidic friction. When one passes an electric current through an electrolyte solution, one also observes a rise in its temperature. This is because the electric field adds (electric) potential energy to it, which then turns into its thermal energy. This phenomenon is known as Joule (or Ohmic) heating. These are examples of the commonly seen degradation of mechanical (i.e., kinetic and potential) energy into internal (or thermal) energy in fluids. It appears to be widely believed without proof that the reverse process does not occur in many cases as a result of the second law of thermodynamics. It is, however, not well known theoretically under what conditions this irreversible conversion of mechanical into internal energy is indeed true.

The purpose of the present article is to clarify such conditions in light of thermodynamics. Actually, in a previous paper,7 it was demonstrated on the basis of the second law that the internal energy of a fluid is not converted into its mechanical energy by itself (when a new thermodynamic theory on nonequilibrium phenomena was advanced). In view of its thermodynamic significance, we present in this article a more definite version of this demonstration in a different manner, answer the above question, and describe its applications in detail.

All that is needed in the analysis to be developed below is familiar balance equations for mass and energy and several usual thermodynamic relations (all of the latter are to be deduced in the Appendix). These equations and relations are applied to each local point in a fluid system.

The rest of the article is organized as follows. In Section 2.1, we take up balance equations for mass and internal energy in fluids and examine the latter from a thermodynamic point of view, resulting in an exact expression for the interconversion of mechanical and internal energy, instead of a customary but inadequate one. In Section 2.2, from the balance equations in...
Section 2.1 and the Gibbs relation we derive a balance equation for entropy, the source term of which represents the entropy production, i.e., the rate of change in entropy produced inside a fluid system. In Section 2.3, we prove from the expressions in Sections 2.1 and 2.2 that the mechanical energy of a fluid necessarily converts into its internal energy provided that the fluid is thermodynamically uniform, by hypothesizing that the entropy production is always positive in accordance with the second law of thermodynamics. In Section 3, the proof is corroborated by looking closely into the two experimental instances stated above. Section 3 also deals with a case in which the internal energy can actually be transformed into the mechanical energy. Section 4 contains a few new observations on this study.

2. RESULTS

2.1. Balance Equations for Mass and Internal Energy.

We consider a fluid (i.e., liquid or gas) system consisting of $n$ components (i.e., chemical species), among which $r$ chemical reactions take place. (Chemical reactions are included here for completeness. In light of practical applications, however, their descriptions in what ensues may be disregarded at the discretion of the reader.) Although solid systems (e.g., metals) are not specifically treated, some of the results obtained below may also be applicable to them. The time rates of change of mass and internal energy at each location of the system are described by their balance equations

$$\frac{d\rho_i}{dt} = -\nabla \cdot (\rho_i \mathbf{v}_i) + \sum_{j=1}^{r} \nu_{ij} M_j \mathbf{u}_j$$

(1)

$$\frac{d\tilde{u}_i}{dt} = -\nabla \cdot (\tilde{u}_i + \mathbf{v}) - P_i \nabla \mathbf{v} + \sum_{j=1}^{n} \mathbf{J}_j$$

(2)

where $t$ is the time; $\rho_i$, $\mathbf{v}_i$, and $M_i$ are the partial density, velocity, and molar mass of component $i$, respectively, with $\mathbf{v}$ measured with respect to a coordinate system fixed to the container of the fluid; $\tilde{u}_i$, $\mathbf{J}_j$, $P_i$, and $\mathbf{v}$ are, respectively, the internal energy density (i.e., per unit volume), heat flow, stress tensor, and velocity of the center of mass

$$\mathbf{v} = \frac{1}{\rho} \sum_{i} \rho_i \mathbf{v}_i$$

(3)

with $\rho$ the total density

$$\rho = \sum_{i} \rho_i$$

(4)

$\mathbf{J}_j$ is the diffusion flow of component $i$ relative to the center of mass

$$\mathbf{J}_j = \rho_i (\mathbf{v}_i - \mathbf{v})$$

(5)

and $F_i$ is an external force per unit mass exerted on component $i$ and is derived from a potential $\psi_i$ (electric, gravitational, etc.)

$$F_i = -\nabla \psi_i$$

(6)

In eq 1, $\nu_{ij}$ is the stoichiometric coefficient of component $i$ in chemical reaction $j$, which is positive or negative according to whether it is a net product or reactant, respectively, in the reaction. The quantity $\nu_{ij}$ is the rate of reaction $j$ in terms of moles per unit volume and unit time. In eq 2, the colon between $P$ and $\nabla \mathbf{v}$ signifies their double dot (or scalar) product.

We now need to obtain from eq 2 an expression for the (rate per unit volume of) interconversion of mechanical and internal energy. If eq 2 were properly separated into the negative divergence of a flow of internal energy and a source term, then the latter (i.e., $-P_i \nabla \mathbf{v} + \sum_{j} \mathbf{J}_j F_i$ here) would become such an expression. Actually, the separation in eq 2 has not undergone a close thermodynamic scrutiny, so that its validity is not guaranteed, albeit eq 2 as a whole is accurate. To pursue this question, we apply to each position of the system a thermodynamic relation for the time change of internal energy (see the Appendix for its deduction)

$$\frac{d\tilde{u}_i}{dt} = \tilde{c}_f \frac{dT}{dt} - \alpha T \frac{dp}{dt} + \sum_{i} h_i \frac{dh_i}{dt}$$

(7)

where $\tilde{c}_f$ is the heat capacity at constant pressure per unit volume, $T$ the absolute temperature, $\alpha$ the expansion coefficient at constant pressure, $p$ the pressure, and $h_i$ the partial specific enthalpy of component $i$. As shown below, eq 7 allows us to identify the true flow of internal energy and hence the correct expression for the energy conversion. The first term on the right-hand side of eq 7 represents the temperature variation in enthalpy per unit volume at constant pressure and composition (cf. eq A.1 in the Appendix). It therefore involves the heat flow $\mathbf{J}_q$ or, more precisely, its negative divergence. In multicomponent systems, however, $\mathbf{J}_q$ generally includes a heat flow $\sum_i h_i \mathbf{v}$ attributed to diffusion, which is to be excluded from $\mathbf{J}_q$. The term $\tilde{c}_f \frac{dT}{dt}$ thus has the heat flow $\mathbf{J}_q - \sum_i h_i \mathbf{v}$ due to pure conduction. In consideration of the mass balance eq 1, the last term of eq 7 produces the term

$$-h_i \nabla \cdot (\rho_i \mathbf{v}_i) = -\nabla \cdot (\rho_i \mathbf{v}_i) + \rho_i \mathbf{v} \cdot \nabla \mathbf{v}_i$$

(8)

and hence contains the enthalpy flow due to transport of matter, $\sum_i \rho_i \mathbf{v}$. Consequently, the internal energy flow $\mathbf{J}_u$ pertinent to the balance eq 2 should be

$$\mathbf{J}_u = \mathbf{J}_q - \sum_i h_i \mathbf{v} = \mathbf{J}_q + \mathbf{h}$$

(9)

but not $\mathbf{J}_q + \tilde{u}$, as suggested from eq 2. In eq 9, account has been taken of eq 5 and the thermodynamic relation

$$\sum_i h_i \rho_i = \mathbf{h}$$

(10)

where $\mathbf{h}$ is the enthalpy density. With eq 9, eq 2 can be rewritten as

$$\frac{d\tilde{u}_i}{dt} = -\nabla \cdot (\mathbf{J}_q + \mathbf{h}) + \rho_i \mathbf{v} \cdot \nabla \mathbf{v}_i - P_i \nabla \mathbf{v} + \sum_{j} \mathbf{J}_j F_i$$

(11)

where we have used the relation

$$\mathbf{h} = \tilde{u} + p$$

(12)

and have assumed that the stress tensor $\mathbf{P}$ can be divided into the pressure and the viscous stress tensor $\mathbf{\Pi}$

$$\mathbf{P} = p I + \mathbf{\Pi}$$

(13)

where $I$ is the unit tensor. (Throughout this article, the pressure $p$ corresponds to the thermodynamic pressure of a fluid at rest, which is supposed to obey the same forms of thermodynamic relations as in thermal equilibrium. It generally differs from the mechanical pressure actually acting on the fluid in motion. The
effects of the difference are included in the viscous stress tensor \( \Pi \), although they are negligible, e.g., for incompressible fluids with small velocity gradients. For more information, see, e.g., ref 11. In the present treatment, these two pressures are regarded as equal because what is called local equilibrium is presupposed; see the Appendix.) The quantity \( \Phi \) in eq 11 is the interconversion of energy given by

\[
\Phi = v \cdot \nabla p - \Pi : \nabla v + \sum_i J_i \vec{F}_i
\]  

(14)

which is the desired result expressing the conversion of mechanical energy into internal energy per unit volume and unit time. Equation 11 may thus be more appropriate in form than the customary eq 2 as a balance equation for internal energy.

It may be relevant here to dwell on the physical significance of \( J_u \) and \( \Phi \). Equation 9 states that the energy flow \( J_u \) is composed of the heat flow \( J_u \) and the enthalpy flow \( h \nu \) due to the center of mass motion, i.e., convection. Another interpretation of possible by rewriting eq 9 as

\[
J_u = \sum_i u_i \rho_i \gamma_i + \left( \sum_i h_i J_i \right) + p \sum_i \nu_i \phi_i
\]  

(15)

where use has been made of the relation

\[
h_i = u_i + p v_i
\]  

(16)

with \( u_i \) and \( v_i \) the partial specific internal energy and volume, respectively, of component \( i \). The three terms on the right-hand side of eq 15 designate, respectively, the flow of internal energy due to matter transport, the pure heat flow, and the work done by the pressure on a flowing volume \( \sum \nu_i \phi_i \). In traditional (i.e., equilibrium) thermodynamics, the internal energy of a closed system is varied by the work done by the pressure on a changing volume. The last term in eq 15 thus represents a natural generalization of such work to flow systems. (This term may also be termed "generalized flow work", given that the quantity \( pv \) is often called flow work.)

As stated in connection with eq 9, the flow \( J_u \) of internal energy includes the enthalpic contribution \( \sum h_i \rho_i \gamma_i \), ascribable to matter transfer. This result is consistent with a thermodynamic analysis conducted by Knieman, Barneveld, and Besseling,\(^{12}\) who have shown that when component \( i \) enters an open system by an infinitesimal mass \( dm_i \), the internal energy of the system changes by the amount \( h_i dm \). It should be emphasized that this important point had been overlooked in the literature and that, therefore, even a number of otherwise excellent textbooks on chemical thermodynamics need to be revised in relation to the treatment of open systems in general, as pointed out in ref 12.

The energy conversion \( \Phi \), on the other hand, also has three kinds of contributions. The first term on the right-hand side of eq 14 describes the conversion when the center of mass moves in the presence of a pressure gradient. When the motion is in the direction of increasing pressure, the kinetic energy turns into the internal energy, whereas when the motion is in the direction of decreasing pressure, the reverse holds true. [Alternatively, the quantity \(-v \cdot \nabla p\) may be viewed as representing the work carried out per unit time and unit volume by the pressure on a small volume element moving with the fluid. If this quantity is positive (negative), then it leads to an increase (a decrease) in kinetic energy and a decrease (an increase) in internal energy.] The second term in eq 14 refers to the conversion of kinetic into internal energy attributable to viscosity. The last term of eq 14 denotes the work performed by external forces in the direction of diffusion currents, by which amount the potential energies due to the external forces are reduced and internal energy is created.

2.2. Entropy Balance Equation. To incorporate the second law of thermodynamics into our treatment, we need to derive a balance equation for entropy. To this aim, we utilize the Gibbs relation as adapted to each point (see the Appendix)

\[
\frac{\partial s}{\partial t} = \frac{\partial a}{\partial t} - \sum_i \mu_i \frac{\partial \rho_i}{\partial t}
\]  

(17)

where \( \delta \) is the entropy density and \( \mu_i \) is the specific chemical potential (or partial specific Gibbs free energy) of component \( i \).

Substitution of eqs 1 and 11 into eq 17 and division of the result by \( T \) yields

\[
\frac{\partial s}{\partial t} = \frac{1}{T} \left[ -\nabla \cdot J_u + \Phi + \sum_i \mu_i \nabla \cdot (\nu_i \phi_i) + \sum_i w_i A_i \right]
\]  

(18)

where \( A_i \) is the chemical affinity of reaction \( \gamma \)

\[
A_i = -\sum \nu_i M \mu_i
\]  

(19)

To express eq 18 as the negative divergence of a flow of entropy and a source term, we employ a thermodynamic relation for the time variation of entropy (see the Appendix again)

\[
\frac{\partial s}{\partial t} = \nabla \cdot \nabla \frac{T}{T} = -\frac{\partial p}{\partial t} + \sum_i s_i \frac{\partial s_i}{\partial t}
\]  

(20)

where \( s_i \) is the partial specific entropy of component \( i \). We proceed in a way similar to that the energy balance eq 11 was deduced. Let us examine what flows are involved in the right-hand side of eq 20. As explained in Section 2.1, since the quantity \( \nabla \cdot \frac{T}{T} \) contains the (pure) heat flow \( J_u - \sum_i h_i J_i \), the first term on the right-hand side of eq 20 gives the term

\[
-\frac{1}{T} \nabla \left( \frac{J_u - \sum_i h_i J_i}{T} \right) = -\nabla \left( \frac{J_u}{T} - \sum_i \frac{h_i J_i}{T} \right) + \frac{1}{T} \nabla \left( \frac{1}{T} \right)
\]  

(21)

and hence the entropy flow due to that heat flow, \( (J_u - \sum_i h_i J_i)/T \). As the last term of eq 7 has the flow \( \sum h_i \rho_i \gamma_i \) (see eq 8), so the last term of eq 20 has \( \sum \nu_i \phi_i \), the entropy flow due to matter transport. The total entropy flow \( J_s \) thus becomes

\[
J_s = \frac{J_u}{T} - \sum_i \frac{h_i J_i}{T} + \sum_i \nu_i \phi_i = \frac{J_u}{T} - \sum_i \mu_i \rho_i \gamma_i
\]  

(22)

where we have used the first equality in eq 9 and the thermodynamic relation

\[
\mu_i = h_i - T s_i
\]  

(23)

With eq 22, eq 18 leads to the required entropy balance equation

\[
\frac{\partial s}{\partial t} = -\nabla \cdot \left( \frac{J_u}{T} - \sum_i \mu_i \rho_i \gamma_i \right) + J_u \cdot \nabla \left( \frac{1}{T} \right) + \Phi \frac{1}{T}
\]

\[
- \sum_i \rho_i \gamma_i \nabla \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum w_i A_i = -\nabla \cdot J_s - \sigma
\]  

(24)
where \( \sigma \) is the source of entropy, normally termed the (rate of) entropy production (per unit volume), and is given by
\[
\sigma = \mathbf{J}_i \cdot \nabla \left( \frac{1}{T} \right) + \frac{\Phi}{T} - \sum_i \rho_i \mathbf{V} \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum_j w_j A_j.
\] (25)

It may be added for later reference that eq 25 can be brought into another form with the aid of the Gibbs–Duhem relation (see the Appendix)
\[
\Sigma \mathbf{V} \left( \frac{1}{T} \right) + \frac{\nabla p}{T} - \sum_i \rho_i \mathbf{V} \left( \frac{\mu_i}{T} \right) = 0
\] (26)

Taking the scalar product of this relation with the velocity \( \mathbf{v} \) and subtracting the result from eq 25, bearing eqs 5 and 14 in mind, we get
\[
\sigma = \mathbf{J}_i \cdot \mathbf{v} \left( \frac{1}{T} \right) - \frac{1}{T} \Pi : \mathbf{v} = \frac{1}{T} \sum_i J_i - \sum_i J_i \cdot \mathbf{v} \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum_j w_j A_j.
\] (27)

This form for the entropy production more often appears in textbooks on nonequilibrium thermodynamics (see, e.g., refs 8 and 10).

2.3. Conditions for Interconversion between Mechanical and Internal Energy. We now introduce the second law of thermodynamics. It originally states that for a closed system, which can exchange heat but not matter with its surroundings, the change in entropy associated with irreversible processes inside the system is always positive. We postulate that this also holds good at any point in a nonequilibrium system. It is thus required that the local entropy production be positive definite
\[
\sigma > 0
\] (28)

With this inequality, eq 25 becomes
\[
\sigma = \mathbf{J}_i \cdot \mathbf{v} \left( \frac{1}{T} \right) + \frac{\Phi}{T} - \sum_i \rho_i \mathbf{V} \left( \frac{\mu_i}{T} \right) + \frac{1}{T} \sum_j w_j A_j > 0
\] (29)

Let us now consider what this relation implies. It is seen that the entropy production comprises four parts depicting separate nonequilibrium processes. They are the flow of internal energy in the presence of a temperature gradient, the interconversion of mechanical and internal energy, the flows of substances subject to the gradients of thermodynamic variables, and chemical reactions. It follows from the inequality 29 that if the energy conversion is the only process present or predominates over other processes, then \( \Phi \) is always positive. That is, the mechanical energy is necessarily transformed into the internal energy; the reverse never happens. This is especially the case when the system is uniform in temperature, pressure, and composition and no chemical reaction occurs, in which case \( \nabla (1/T) = 0, \nabla (\mu_i/T) = 0, \) and \( w_j = 0 \) in the inequality 29. If, on the other hand, other processes (i.e., heat flow, matter flow accompanied by thermodynamic variable gradients, or chemical reactions) are comparable to the energy conversion, then \( \Phi \) can be negative, i.e., the internal energy can be converted into the mechanical energy. These conditions may be paraphrased (in a less restricted manner) as “if the system is not uniform in temperature, pressure, or composition, or if a chemical reaction takes place”. We will address at the end of Section 3, a typical case that actually exhibits the conversion of internal into mechanical energy. (The implications of the terms other than \( \Phi/T \) in the inequality 29 are provided in ref 7.)

3. DISCUSSION

To better understand the foregoing proof in Section 2.3, we illustrate it with the two experimental examples referred to in Section 1. In the first example, we assume that the fluid is well stirred so that it is thermodynamically uniform. The expressions 14 and 29 then become
\[
\Phi = -\Pi : \mathbf{v} \mathbf{v}
\] (30)
\[
\sigma = -\frac{1}{T} \Pi : \mathbf{v} \mathbf{v} > 0
\] (31)

The positiveness of the entropy production \( \sigma \) therefore means that of the energy conversion \( \Phi \) as well. In other words, the mechanical (or kinetic) energy always turns into the internal energy, not the other way around. We further assume that the stirring of the fluid is sufficiently uniform spatially in such a way that the divergence of the internal energy flow \( J_i = J_i + \mathbf{h} \mathbf{v} \) is negligibly small compared to \( \Phi \). The energy balance 11 then reduces to
\[
\frac{\partial h}{\partial t} = -\nabla \cdot (\Phi \mathbf{v} + \mathbf{J}) \approx \Phi = -\Pi : \mathbf{v} \mathbf{v}
\] (32)

The internal energy thus increases at every position in the system, which leads to a rise in temperature, as is observed experimentally. (Strictly speaking, this temperature rise may be explained by means of a stability condition for local equilibrium, which is an indirect consequence of the second law of thermodynamics; see ref 7, particularly the inequality 45 therein.) The quantity \( -\Pi : \mathbf{v} \mathbf{v} \) in eq 32 corresponds to the “fluidic friction” mentioned in Section 1. Figure 1 summarizes the balance between the kinetic and internal energies for this case.

![Figure 1. Energy changes per unit time and unit volume at each point in a well-stirred fluid. \( \Pi \): viscous stress tensor and \( \mathbf{v} \): fluid velocity.](https://dx.doi.org/10.1021/acsomega.0c02691)

As an exemplification of the validity of our argument, suppose that the fluid can be described as a Newtonian fluid. It is the simplest model of fluids that applies to many ordinary fluids, e.g., water and air, under usual circumstances. For a Newtonian fluid, the components of the viscous stress tensor \( \Pi \) are given in rectangular coordinates by
\[
\Pi_{ij} = -\eta \left( \frac{\partial v_j}{\partial x_i} + \frac{\partial v_i}{\partial x_j} \right) + \left( \frac{2}{3} \eta - \zeta \right) (\nabla \cdot \mathbf{v}) \delta_{ij}
\] (33)

where \( \eta \) and \( \zeta \) are the viscosity and bulk (also known as volume or dilational) viscosity, respectively, both of which are positive quantities; the indices \( i \) and \( j \) take on the values 1, 2, 3 referring to the three coordinate axes; \( v_i \) is a component of the velocity \( \mathbf{v} \); \( x_i \) is a position coordinate; \( \delta_{ij} \) is the Kronecker delta, which is 1 for \( i = j \) and zero for \( i \neq j \). It follows from eq 33 that...
\[-\Pi \cdot \nabla v = - \sum_{i=1}^{3} \sum_{j=1}^{3} \Pi_{ij} \frac{\partial v_j}{\partial x_i} \]
\[= \frac{\eta}{2} \sum_{i} \left( \frac{\partial v_i}{\partial x_i} + \frac{\partial v_i}{\partial x_j} \right) - \frac{2}{3} (\nabla \cdot v) \delta_i \]
\[+ \zeta (\nabla \cdot v)^2 \]

which is always positive. The positivity of \( \sigma \) and \( \Phi \) is thus validated for Newtonian fluids.

Incidentally, if in the case under consideration, we employ the conventional eq 2 of internal energy as such, the energy conversion \( \Phi' \) reads
\[\Phi' = -P \cdot \nabla v = -p \nabla \cdot v - \Pi \cdot \nabla v \]

While the last term \( -\Pi \cdot \nabla v \) is positive definite, the term \( p \nabla \cdot v \) may be either positive or negative depending on whether the fluid is being expanded or compressed. The conversion \( \Phi' \) can therefore be negative in principle unless the fluid is completely incompressible, in which case \( \nabla \cdot v = 0 \). That is, the internal energy can be transformed into the kinetic energy, which may be in contradiction to our ordinary experiences. This fact is another reason why the accustomed energy eq 2 is not reliable as is.

In the second example of Joule heating, let us suppose that a spatially uniform electric field is imposed on a uniform electrolyte solution. As a result, each ion and hence the center of mass will have a velocity uniform in space if any. We then see from the expressions 14 and 29 that
\[\Phi = \sum_i J_i \cdot F_i \]
\[\sigma = \frac{1}{T} \sum_i J_i \cdot F_i > 0 \]

It thus turns out that if \( \sigma > 0 \), then \( \Phi > 0 \), indicating that the electric potential energies irreversibly convert into the internal energy. In the situation under study, the flow \( J_i \) is also uniform in space. We therefore have, as in eq 32
\[\frac{d\tilde{\Phi}}{dt} = \Phi = \sum_i J_i \cdot E \]

Accordingly, the internal energy and hence the temperature increases at every location, in agreement with experimental observations.

By way of illustration of the above results, eqs 36 and 37 may be rewritten as
\[\Phi = I \cdot E \]
\[\sigma = \frac{1}{T} I \cdot E \]

where \( I \) is the electric current density and \( E \) is the electric field. This is because the external force \( F_i \) and \( I \) are given by
\[F_i = z_i E \]
\[I = \sum_i z_i J_i \]

where \( z_i \) is the charge per unit mass of component \( i \). Figure 2 shows the balance between the electric potential energy and internal energy in this system. When Ohm’s law (in differential form)

\[I = \kappa E \]

applies, where \( \kappa \) is the specific conductance, we indeed find that \( \sigma > 0 \) and \( \Phi > 0 \). Expressed as eq 39, \( \Phi \) represents the so-called Ohmic heat (in differential form) per unit time.\(^6\)

The preceding discussion pertains to the time variation in internal energy at a local point. We now focus on that of a fluid system as a whole, in which we assume that convective motion and the interconversion of energy can take place. In that case, the local entropy production is, from the relations 27 and 28
\[\sigma = -\frac{1}{T} \Pi \cdot \nabla v + \frac{1}{T} \sum_i J_i \cdot F_i > 0 \]

Integrating the energy balance 11 over the volume \( V \) of the system and utilizing Gauss’s divergence theorem, we get
\[\frac{dU}{dt} = \int \frac{d\tilde{\Phi}}{dt} dV = -\int \sum_i (J_i + \tilde{f} v) \cdot d\Omega + \int \Phi dV \]

where \( U \) is the internal energy of the entire system, \( \Omega \) is the surface encircling the system, and \( d\Omega \) is a vector with the magnitude of a surface area element \( d\Omega \) and oriented normal to and outward from it. For simplicity, the system is assumed to be isolated, i.e., it exchanges neither energy nor matter with its environment. The first term on the far right-hand side of eq 45 then vanishes, reducing it to
\[\frac{dU}{dt} = \int \Phi dV \]

On the other hand, if the external force \( F_i \) is independent of time, the total energy of the system is conserved
\[\frac{dU}{dt} + \frac{d(K + P)}{dt} = 0 \]

where \( K \) and \( P \) are the kinetic and potential energies of the system, respectively. (Note that the velocity \( v \) and hence the kinetic energy in this equation is determined relative to the vessel that contains the fluid.) If the system is uniform in pressure, eq 14 and the inequality 44 yield
\[\Phi = -\Pi \cdot \nabla v + \sum_i J_i \cdot F_i > 0 \]

It thus follows from this inequality and eqs 46 and 47 that the internal energy of the whole system increases and its mechanical energy \( K + P \) decreases with time.

If the pressure is not uniform within the system, on the other hand, \( \Phi \) as given by eq 14 can be negative despite the inequality 44, in which case the internal energy of the system can decrease temporarily. To exemplify such behavior, let us imagine that two fluids are filled in an adiabatic container and separated by a partition, as portrayed in Figure 3. The two fluids contain a single constituent of the same kind at the same temperature but at different pressures. We examine what will happen when the...
When the partition is removed, the left fluid will flow into the right and they will ultimately form a uniform fluid, as shown in (b).

At the instant of the removal of the partition, when \( v = 0 \) everywhere, the equation of motion of the fluid reduces to \(^8,9\)

\[
\rho \frac{dv}{dt} = -\nabla p
\]

at the boundary between the two fluids. As expected, eq 51 indicates that the fluid starts moving from the higher to lower pressure, which makes the term \( \nabla p \) in eq 49 negative around the boundary. On the other hand, it may be seen from eq 47 with \( P \equiv 0 \) that at least initially, \( dU/dt < 0 \) and \( dK/dt > 0 \), i.e., the internal energy is converted into the kinetic energy, since the two fluids were stationary at first and hence had no kinetic energy. These results, together with the expressions 46, 49, and 50, imply that at an early stage, \( \nabla Vp \) is larger than \( -\Pi : \nabla v \) in regions where the two fluids are in contact with each other. As the fluid flows in the direction of decreasing pressure, the pressure gradient and hence the velocity will gradually diminish, which will make \( \nabla Vp \) dwindle faster than \( -\Pi : \nabla v \). The former will therefore eventually become smaller than the latter, with the result that \( \Phi \) and \( dU/dt \) become positive. The kinetic energy then turns into the internal energy. This process will continue until the kinetic energy is exhausted, when the pressure is uniform throughout the container. In that case, a new equilibrium state has been established, with its total internal energy equal to the sum of the internal energies that the two fluids had before the partition was taken away, since the overall system is thermally insulated. The time course of the total internal energy (\( U \)) and total kinetic energy (\( K \)) is outlined in Figure 4.

Figure 3. (a) Two identical pure fluids of the same temperature are separated by a partition in an adiabatic container, with the left fluid having a higher pressure (or density) than the right. When the partition is removed, the left fluid will flow into the right and they will ultimately form a uniform fluid, as shown in (b).

4. CONCLUSIONS

In this article, we have investigated in what situations the mechanical energy of a fluid turns into its internal energy or not. As a result, we have found that the irreversible transformation of mechanical into internal energy is possible provided that the fluid is uniform in temperature, pressure, and composition. If the fluid is not uniform in either of these properties, then its internal energy can be transformed into its mechanical energy. These new findings are by no means trifling or self-evident; they can be deduced only when thermodynamics, particularly its second law, is applied carefully to the matter at hand (see also the next paragraph). In this respect, we realize that this law, originally formulated for processes between equilibrium states, is powerful in predicting the behavior in nonequilibrium systems as well.

Now that these results have been placed on a firm thermodynamic footing, they may safely be quoted when dealing with energy conversion in general or applications of the second law, or even when teaching thermodynamics in classrooms. They may also bear relevance to the study of such natural phenomena as mentioned in Section 1.3–6.

One might wonder why such a basic and instructional problem had not been solved long before, in view of the availability of the constituent equations involved. This may be partly because the energy balance concerned had previously not been treated adequately. In fact, if the problem is approached along the lines of the conventional energy eq 2, one is confronted with undesirable consequences, as explained in connection with eq 35. Instead, the correct form 11 should be invoked to obtain consistent results.

It may finally be remarked that what this article is concerned with is the interconversion of energy in a single substance. If two or more substances are combined, the internal energy of a fluid may be freely transformed into the mechanical energy of others.

A good example is a heat engine, where the internal energy of a working fluid is increased by applying heat and then converted into the mechanical energy of a suitable device, such as a piston or turbine blade.

APPENDIX: DERIVATION OF NECESSARY THERMODYNAMIC RELATIONS (EQS 7, 17, 20, AND 26)

In this appendix, we first derive some pertinent thermodynamic relations valid at equilibrium. They are then adapted to a local point in a nonequilibrium system to obtain requisite expressions for the analysis in the body of the article.

Let us consider an open uniform system that exchanges energy and matter with its surroundings and how its thermodynamic quantities vary between its equilibrium states under the influence of the exterior. Such variations are assumed to be infinitesimally small and are designated by the symbol \( \delta \).

We first express the change in the internal energy density (i.e., per unit volume) \( u \) in terms of the temperature \( T \), pressure \( p \), and partial density \( \rho_i \). To this end, it is expedient to note that the change in the enthalpy \( H \) of the system may be written as
\[
\delta H = \left( \frac{\partial H}{\partial T} \right)_{p, \{m_i\}} \delta T + \left( \frac{\partial H}{\partial p} \right)_{T, \{m_i\}} \delta p + \sum_i \left( \frac{\partial H}{\partial m_i} \right)_{T, p, \{m_{\neq i}\}} \delta m_i
\]

where \( m_i \) is the mass of component \( i \) in the system; the subscripts \( \{m_i\} \) and \( \{m_{\neq i}\} \) denote that every mass and every mass except \( m_i \) are kept fixed, respectively; \( C_p \) is its heat capacity at constant pressure; \( V \) its volume; \( \alpha \) the expansion coefficient at constant pressure

\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{p, \{m_i\}}
\]

and \( h \) the partial specific enthalpy of component \( i \). Since the enthalpy \( H \) is defined from the internal energy \( U \) by

\[
H = U + pV
\]

we have

\[
\delta H = \delta U + V \delta p + p \delta V \tag{A.4}
\]

Identification of the right-hand sides of eqs A.1 and A.4 gives

\[
\delta U = C_p \delta T - \alpha V \delta p - p \delta V + \sum_i h_i \delta m_i \tag{A.5}
\]

If we use the definitions

\[
\bar{u} = \frac{U}{V}, \quad \rho_i = \frac{m_i}{V} \tag{A.6}
\]

then

\[
\delta \bar{u} = \frac{1}{V} \delta U - \frac{\delta V}{V} U, \quad \delta \rho_i = \frac{1}{V} \delta m_i - \frac{\delta V}{V} m_i \tag{A.7}
\]

It follows from eqs A.3, A.5, and A.7 and the thermodynamic relation

\[
H = \sum_i h_i m_i \tag{A.8}
\]

that

\[
\delta \bar{u} - \bar{c}_p \delta T + \alpha \bar{T} \delta p - \sum_i h_i \delta \rho_i = \frac{1}{V} \left( \delta U - C_p \delta T + \alpha V \delta p + p \delta V - \sum_i h_i \delta m_i \right)
\]

\[
- \frac{\delta V}{V} \left( U + pV - \sum_i h_i m_i \right) = 0 \tag{A.9}
\]

where \( \bar{c}_p = C_p / V \) is the heat capacity per unit volume. Thus

\[
\delta \bar{u} = \bar{c}_p \delta T - \alpha \bar{T} \delta p + \sum_i h_i \delta \rho_i \tag{A.10}
\]

This is the intended expression.

We now introduce one form of a fundamental thermodynamic relation, i.e., the Gibbs formula, which reads

\[
T \delta S = \delta U + p \delta V - \sum_i \mu_i \delta m_i \tag{A.11}
\]

where \( S \) is the entropy of the system and \( \mu_i \) is the specific chemical potential (or partial specific Gibbs free energy) of component \( i \). On this basis, we deduce a relation involving the change in the entropy density

\[
\delta \bar{s} = \frac{1}{V} \frac{\delta S}{V} - \frac{\delta V}{V^2} S \tag{A.12}
\]

from which

\[
T \delta \bar{s} = \delta \bar{u} - \sum_i \mu_i \delta \rho_i \tag{A.15}
\]

where use has also been made of the thermodynamic relation

\[
U + pV - TS = H - TS = G = \sum_i \mu_i m_i \tag{A.16}
\]

with \( G \) the Gibbs free energy of the system. Equation A.15 is the desired relation.

The change in \( S \) may also be expressed as

\[
\delta S = \left( \frac{\partial S}{\partial T} \right)_{p, \{m_i\}} \delta T + \left( \frac{\partial S}{\partial p} \right)_{T, \{m_i\}} \delta p + \sum_i \left( \frac{\partial S}{\partial m_i} \right)_{T, p, \{m_{\neq i}\}} \delta m_i - \frac{\delta V}{V} \left( TS - U - pV \sum_i \mu_i m_i \right) = 0 \tag{A.17}
\]

where \( s_i \) is the partial specific entropy of component \( i \). We then proceed as in eq A.9 or eq A.14 and utilize the thermodynamic relation

\[
S = \sum_i s_i m_i \tag{A.18}
\]

arriving at

\[
\delta \bar{s} = \bar{c}_p \delta T - \alpha \bar{T} \delta p + \sum_i s_i \delta \rho_i \tag{A.19}
\]

This equation can also be obtained by inserting eq A.10 into eq A.15, dividing the result by \( T \), and taking into account the thermodynamic relation
\( \mu = h_0 - T_s \)  \hspace{1cm} (A.20)

Finally, we aim at gaining a Gibbs–Duhem relation. Division of eq A.16 by \( TV \) gives

\[
\frac{\delta h}{T} = \sum_i \frac{\mu_i}{T} \rho_i
\]

where \( \delta h = H/V \) is the enthalpy density. For infinitesimal variations, we have from eq A.21

\[
\frac{\delta h}{T} + \frac{\delta \bar{h}}{T} - \delta \bar{s} = \sum_i \rho_i \frac{\delta (\frac{H_i}{T})}{T} + \sum_i \mu_i \delta \rho_i
\]

If, on the other hand, eq A.3 as divided by \( V \), i.e.,

\[
\bar{h} = \bar{u} + p
\]

is employed in eq A.15 and the result is divided by \( T \), we get

\[
\delta \bar{s} = \frac{\delta h}{T} - \frac{\delta p}{T} - \sum_i \mu_i \delta \rho_i
\]

Substitution of eq A.24 into eq A.22 leads to

\[
\frac{\delta h}{T} \left( \frac{1}{T} + \frac{\delta p}{T} \right) - \sum_i \rho_i \frac{\delta (\mu_i/T)}{T} = 0
\]

which is one form of the Gibbs–Duhem relation.

To apply these relations to nonequilibrium situations, we now hypothesize that the spatial variations of thermodynamic quantities in a nonequilibrium system are not too large and that their temporal variations are slow compared to the time needed for microscopic processes in the system to relax so as to realize their macroscopic averages. In such circumstances, their gradients and time variations may be expected to follow the same forms of thermodynamic relations as in equilibrium. (Such an assumption is usually called the hypothesis of local equilibrium.) We may thus replace the operator \( \delta \) in the above expressions with either the gradient \( \nabla \) or the time derivative \( \partial \)/\( \partial t \) at a fixed position. For instance, we have from eqs A.10, A.15, A.19, and A.25

\[
\frac{\partial \bar{u}}{\partial t} = \bar{c}_p \frac{\partial T}{\partial t} - \alpha T \frac{\partial p}{\partial t} + \sum_i h_i \frac{\partial \rho_i}{\partial t}
\]

\[
T \frac{\partial \bar{s}}{\partial t} = \frac{\partial \bar{u}}{\partial t} - \sum_i \mu_i \frac{\partial \rho_i}{\partial t}
\]

\[
\frac{\partial \bar{s}}{\partial t} = \bar{c}_p \frac{\partial T}{\partial t} - \alpha \frac{\partial p}{\partial t} + \sum_i \frac{\partial \rho_i}{\partial t}
\]

\[
\bar{h} \nabla \left( \frac{1}{T} \right) + \frac{\nabla p}{T} - \sum_i \rho_i \nabla \left( \frac{\mu_i}{T} \right) = 0
\]

These are, respectively, eqs 7, 17, 20, and 26 in the main text.

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