



aporative and
ynamic Factors
mal Symposium
uence of Down-
irl Atomizers,"
l. 108, p. 219.
nterdependence
," ASME Jour-
39.
s and Particles,
n and Combustion
tion in Sprays,"
The Properties
pany.
stream Distance
nnual Meeting,
ay Combustion
asurements of
id Mass Trans-

W. R. Dunbar

Department of Mechanical and Industrial
Engineering,
Marquette University,
Milwaukee, WI 53233-2286

N. Lior

Department of Mechanical Engineering and
Applied Mechanics,
University of Pennsylvania,
Philadelphia, PA 19104-6315

R. A. Gaggioli

Department of Mechanical and Industrial
Engineering,
Marquette University,
Milwaukee, WI 53233-2286

The Component Equations of Energy and Exergy

Energy conversion processes inherently have associated irreversibility. A better understanding of energy conversion will motivate intuition to create new energy-conversion and energy-utilization technology. In the present article, such understanding is further enhanced by decomposing the equations of energy and exergy (availability, available energy, useful energy) to reveal the reversible and irreversible parts of energy transformations. New definitions of thermal, strain, chemical, mechanical and thermochemical forms of energy/exergy are justified and expressions for these properties and their changes are rigorously developed. In the resulting equations, terms appear which explicitly reveal the interconversions between the different forms of energy/exergy, including the breakdown into reversible and irreversible conversions. The equations are valid for chemically reacting or non-reacting inelastic fluids, with or without diffusion.

Introduction

The traditional set of the equations of change includes the equations of continuity, motion, and energy (e.g., Hirschfelder et al., 1954; Bird et al., 1960). With the relevant kinetic and property relations, this set of differential equations describes mathematically processes undergone by any fluid, wherein the energy transfers are associated with momentum, matter and heat transfers. That is, along with the relevant boundary and/or initial conditions, they constitute a mathematical model of the process. Such a model is of the continuum type, valid provided that the fluid density at each location and time is large enough for an infinitesimal element to qualify as a simple system (Gyftopoulos and Beretta, 1991). The validity of the model also depends upon property relations (and, in turn, kinetic relations) which must take into account a complete set of extensive properties which vary independently.

While the aforementioned equations suffice to *model* (simulate) the processes, in seeking to develop new, more effective technology for transports of and interconversions between the different types of energy, it would be desirable to have explicit equations for each type. In a form which describes the interconversions among types, these equations would provide valuable information for analyzing and, therefore, for managing and controlling the interconversions. That is the objective of this paper, wherein the equations of energy and exergy are decomposed into component equations for kinetic, thermal, strain, and chemical energy/exergy.

In each of these component energy equations the interconversions are broken down into reversible and irreversible parts. As shown by the corresponding component equations for ex-

ergy, the irreversible parts have quantifiable exergy annihilations associated with them.

Indeed, it is the exergy equations which (i) show the desirability for controlling the interconversions, (ii) pinpoint quantitatively the resource expenditures associated with irreversible conversions, and (iii) give insight for discovering prospective means for achieving better utilization of the resources and feedstocks. It is for this reason that the concept of exergy, which goes back to Gibbs (1875) and Maxwell (1872), has been receiving ever-increasing interest, with fruitful applications to numerous energy-conversion and chemical process plants (for example, see Denbigh, 1956; Mah et al., 1977; Umeda et al., 1979; Fan and Shieh, 1980; Ishida and Kawamura, 1982; Moran, 1989; Liu et al., 1983; Tsatsaronis and Winhold, 1985; Szargut et al., 1988).

Existing applications, however, have been to plants and to the devices and units thereof. While there has been some overall analysis of the transport and rate processes within certain devices and units, except for simple viscous dissipations there has been no explicit evaluations of the interconversions occurring within these processes since, heretofore, the basic relationships for analysis of the interconversions have not been available.

To determine the expenditure of exergy (of resources) associated with each interconversion and transport, and hence the relative need for improvement and/or change, the component equations of exergy presented herein will be needed. In turn, to find the means for achieving the improvements and changes, the enhanced quantification provided by the component equations of both energy and exergy will be valuable.

The Equation of Energy

One form of the equation of energy is (e.g., Bird et al., 1960)

Contributed by the Advanced Energy Systems Division and presented at WAM, Atlanta, Georgia, December 1-6, 1991, of THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS. Manuscript received by the AES Division, May 5, 1991; revised manuscript received August 26, 1991.

$$\frac{D}{Dt}(\dot{E}) = -\frac{1}{\rho}(\nabla \cdot q) - \frac{1}{\rho}(\nabla \cdot [\pi \cdot v]) + \frac{1}{\rho} \sum_i (n_i \cdot g_i) \quad (1)$$

In this form, the equation of energy states (Bird et al., 1960) that, for the element of fluid moving with the mass-average velocity, the energy changes because of (i) the net transport of energy by heat conduction and radiation, as well as by diffusion, (ii) the net mechanical transport of energy via stresses, and (iii) the net mechanical transfer of energy via work done on the fluid by body forces. It should be mentioned that the energy E does not include potential energy; the effects of gravitational and other body forces are accounted for by term (iii).

The Equation of Kinetic Energy

By forming the scalar product of the local velocity, v , with the equation of motion, one obtains the equation of kinetic energy (e.g., Bird, 1957; Bird et al., 1960)

$$\frac{D}{Dt}(\dot{K}) = -\frac{1}{\rho}(v \cdot [\nabla \cdot \pi]) + \frac{1}{\rho} \sum_i \rho_i (v \cdot g_i) \quad (2)$$

This relation has also been called "the equation of mechanical energy" (Bird et al., 1960), a name to be reserved in this work for another concept to be presented forthwith.

For inelastic fluids (which cannot sustain a shear stress without deformation), $de = Tds - Pdv + \sum \mu_i d\Omega_i + v \cdot dv$ and the normal stress consists of the thermodynamic and viscous (irreversible) parts: $\pi_n = P\delta + \tau_n$, whereas the shear stress is strictly viscous: $\pi_s = \tau_s$. As will be shown later, when Eq. (2) is rewritten in the following form (by employing the relations $v \cdot \nabla \cdot \pi = \nabla \cdot \pi \cdot v - \pi : \nabla v$ and $n_i = j_i + \rho_i v_i$; Bird et al., 1960), each conversion and transport term can readily be given a straightforward and more meaningful interpretation:

$$\frac{D}{Dt}(\dot{K}) = -\frac{1}{\rho}(\nabla \cdot [\tau_s \cdot v]) + \frac{1}{\rho}(\tau_s : \nabla v) - \frac{1}{\rho}(v \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} \sum_i (n_i \cdot g_i) - \frac{1}{\rho} \sum_i (j_i \cdot g_i) \quad (3)$$

In this form, the equation of kinetic energy states that, for an element of fluid moving with the mass-average velocity, the kinetic energy changes because of (i) the net transport of kinetic energy via shear stresses, (ii) the irreversible conversion of kinetic energy to internal energy via shear stresses (and thus, this term is always nonpositive), (iii) the net reversible interconversion with internal energy, (iv) the net transfer of kinetic energy via the work done on the fluid by body forces, and (v) the portion of the latter transfer which is irreversibly converted to internal energy. This interpretation of the right-hand side of Eq. (3) will be justified later in the paper.

Nomenclature

a = exergy, kJ
 E = energy, kJ
 g = volumetric rate of entropy production, kJ/(°K·m³)
 G = Gibbs free energy (and chemical energy), kJ
 H = enthalpy, kJ
 K = kinetic energy, kJ
 N = mole number
 P = pressure, kPa
 r = chemical species production rate, gmole/s
 R = reaction rate
 S = entropy, kJ/°K

t = time, s
 T = temperature, °K
 U = internal energy, kJ
 v = speed, m/s
 V = volume, m³
 λ = chemical affinity, kJ/gmole
 Ω = mass fraction
 ρ = density, kg/m³
 ν = specific volume, m³/gmole
 μ = chemical potential, kJ/gmole
 ν = stoichiometric coefficient
 f = nonconservative body force per unit mass, kN/kg
 g = body force per unit mass, kN/kg

j = mass diffusion flux (with respect to the mass-average velocity), kg/m²-s
 n = mass diffusion flux (with respect to stationary coordinates), kg/m²-s
 q = energy flux, kJ/m²-s
 v = velocity, m/s
 ϵ = thermal energy flux, kJ/m²-s
 ϕ = potential per unit mass
 σ = entropy flux, kJ/°K-m²-s
 π = pressure tensor, kPa
 τ = shear stress tensor, kPa

The Equation of Internal Energy for Inelastic Fluids

Following the technique employed by Hirschfelder, Curtiss, and Bird (1954), by subtracting the equation of kinetic energy (Eq. (3)) from the equation of energy (Eq. (1)), the resulting relation is a form of the equation of internal energy:

$$\frac{D}{Dt}(\dot{U}) = -\frac{1}{\rho}(\nabla \cdot q) - \frac{1}{\rho}(\nabla \cdot [\pi_n \cdot v]) - \frac{1}{\rho}(\tau_s : \nabla v) + \frac{1}{\rho}(v \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} \sum_i (j_i \cdot g_i) \quad (4)$$

As will be justified later, this form of the equation of internal energy states that, for an element of fluid moving with the mass-average velocity, the internal energy changes because of (i) the net transport of energy by heat conduction and radiation, as well as by diffusion, (ii) the net transport of "strain" energy via normal stresses, (iii) the irreversible conversion of kinetic energy to internal energy via shear stresses, (iv) the net reversible interconversion with internal energy, and (v) the irreversible increase of internal energy via work done on the fluid by body forces.

A Further Decomposition of Energy

In relation to the equation of energy, the equations of internal and kinetic energy offer additional insight, by revealing the interconversions between the "internal" and "external" energy (via the last three terms on the right-hand side of Eq. (4)). Further decomposition of the internal energy is also revealing. The basic relationship to be employed to achieve this is (e.g., Obert, 1960; Denbigh, 1966):

$$U = TS - PV + \sum_i \mu_i N_i \quad (5)$$

There are two other relationships which are important for this decomposition, inasmuch as they allow the interconversions to be classified. The first, the Gibbs-Duhem relation, follows from Eq. (5), the definition of the Gibbs function, and the Gibbs equations (e.g., Denbigh, 1966):

$$SdT - VdP + \sum_i N_i d\mu_i = 0 \quad (6)$$

The other important equation relates the volumetric rate of irreversible entropy production, g , to dissipative conversions (for inelastic fluids; Hirschfelder et al., 1954; De Groot and Mazur, 1962):

$$g = \frac{1}{T} [-(\tau_s : \nabla v) - (\tau_n : \nabla v) - \sum_i (j_i \cdot \nabla(\mu_i - \mu_n)) - (\sigma \cdot \nabla T) + \sum_i \lambda_j R_j + \sum_i (j_i \cdot g_i)] \quad (7)$$

tic Fluids
 der, Curtiss,
 netic energy
 the resulting
 energy:

$$\sum_i (j_i \cdot g_i) \quad (4)$$

on of internal
 ving with the
 es because of
 nd radiation,
 "strain" energy
 on of kinetic
) the net irre-
 l (v) the irre-
 on the fluid

uations of in-
 , by revealing
 d "external"
 d side of Eq.
 gy is also re-
 o achieve this

(5)

important for
 e interconver-
 nem relation,
 function, and

(6)

metric rate of
 e conversions
 De Groot and

($\sigma \cdot \nabla T$)

$$\sum_i (j_i \cdot g_i) \quad (7)$$

(with respect
 velocity),

(with respect
 nates), kg/

kJ/m²-s
 mass
 -m²-s

kPa

of the ASME

The six terms on the right-hand side of Eq. (7) indicate dissipations. The first and second terms are the contributions due to momentum transfer, the third and sixth terms are due to diffusion, the fourth term is due to entropy transfer, and the fifth term is due to chemical reactions.

Further insight is gained by breaking down the internal energy into parts and subsequently developing equations of change for the resulting properties. By definition, the internal energy is mathematically represented by the relation

$$\hat{U} = \hat{E} - \hat{K} = \hat{E} - \frac{v^2}{2} \quad (8)$$

For inelastic fluids, the internal energy is given by Eq. (5), and thus,

$$\hat{E} = \frac{v^2}{2} - Pv + T\hat{S} + \sum_i \mu_i \Omega_i \quad (9)$$

Here, we define each of the four terms on the right-hand side of Eq. (9) to be a distinct kind of energy: the kinetic energy ($v^2/2$), the strain energy ($-Pv$), the thermal energy ($T\hat{S}$), and the chemical energy ($\hat{G} = \sum \mu_i \Omega_i$). The relevant form of the equation of change for kinetic energy is given by Eq. (3). Equations of change for thermal, strain, and chemical energy are developed presently. Such equations contain terms which represent (i) energy transports, (ii) reversible energy interconversions among the various types of energy (e.g., via the Gibbs-Duhem relation), and (iii) irreversible conversions with contribute to the local rate of entropy production (Eq. (7)).

The Equation of Thermal Energy

The equation of kinetic energy was developed by forming a (dot) product of the fluid momentum with the local velocity (the potential conjugate with momentum). In a similar fashion, an equation of thermal energy is developed by multiplying the equation of entropy (e.g., Eq. (11.1-13) of Hirschfelder et al., 1954) by the local temperature T (the potential conjugate with entropy)

$$T \frac{D\hat{S}}{Dt} = -\frac{T}{\rho} (\nabla \cdot \sigma) + \frac{Tg}{\rho} \quad (10)$$

With standard relationships for derivatives of products, Eq. (10) may be rewritten as

$$\frac{D}{Dt} (T\hat{S}) = \hat{S} \frac{DT}{Dt} - \frac{1}{\rho} (\nabla \cdot T\sigma) + \frac{1}{\rho} (\sigma \cdot \nabla T) + \frac{Tg}{\rho} \quad (11)$$

Substitution of Eq. (7) into Eq. (11) results in the desired, new equation of thermal energy which explicitly shows the transport of thermal energy and the interconversions between thermal energy and other kinds of energy:

$$\begin{aligned} \frac{D}{Dt} (T\hat{S}) = & -\frac{1}{\rho} (\nabla \cdot T\sigma) + \hat{S} \frac{DT}{Dt} \\ & + \frac{1}{\rho} [-(\tau_s : \nabla v) - (\tau_n : \nabla v) - \sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) \\ & + \sum_j \lambda_j R_j + \sum_i (j_i \cdot g_i)] \quad (12) \end{aligned}$$

This form the equation of thermal energy states that, for an element of fluid moving with the mass-average velocity, the thermal energy ($T\hat{S}$) changes because of (i) the net transport of thermal energy via diffusion and heat transfer, (ii) the reversible interconversion with strain and/or chemical energy via the Gibbs-Duhem relation (Eq. (6)), and (iii) the irreversible production of thermal energy (a) at the expense of kinetic energy due to shear stress viscous effects, (b) at the expense of strain energy due to normal stress viscous effects, (c) at the expense of chemical energy due to diffusion, (d) at the expense

of chemical energy due to reactions, and (e) at the expense of external sources of energy.

The Equation of Strain Energy

The equation of strain energy is developed by transforming the overall equation of continuity into a "volume balance" and subsequently multiplying this equation by the potential conjugate with volume—the pressure P .

The overall equation of continuity (e.g., Eq. (11.1-2) of Hirschfelder et al., 1954) is

$$\frac{Dv^{-1}}{Dt} = \frac{D\rho}{Dt} = -\rho (\nabla \cdot v) \quad (13)$$

Performing the operation on the left-hand side of Eq. (13) and rearranging results in an alternative form (a volume balance)

$$\frac{Dv}{Dt} = \frac{1}{\rho} (\nabla \cdot v) \quad (14)$$

By multiplying Eq. (14) by the pressure P , and employing the relation $P(\nabla \cdot v) = (\nabla \cdot Pv) - (v \cdot \nabla P) = (\nabla \cdot [\pi_n \cdot v]) - (v \cdot [\nabla \cdot \pi_n]) - (\tau_n : \nabla v)$ and standard relationships for derivatives of products, the resulting relation is the equation of strain energy

$$\begin{aligned} \frac{D}{Dt} (-Pv) = & -\frac{1}{\rho} (\nabla \cdot [\pi_n \cdot v]) - v \frac{DP}{Dt} \\ & + \frac{1}{\rho} (v \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} (\tau_n : \nabla v) \quad (15) \end{aligned}$$

In this form, the equation of strain energy states that, for an element of fluid moving with the mass-average velocity, the strain energy changes because of (i) the net transport of strain energy via normal stresses, (ii) the reversible interconversion with thermal and/or chemical energy via the Gibbs-Duhem relation, (iii) the net reversible interconversion with kinetic energy, and (iv) the irreversible conversion of strain energy to thermal energy via normal stresses.

The Equation of Chemical Energy

The equation of chemical energy is developed by multiplying the equation of continuity of the individual species (e.g., Eq. (11.1-1) of Hirschfelder et al., 1954) by the potential conjugate with material flow, namely, the chemical potential of the relevant species, μ_i

$$\mu_i \frac{D\rho_i}{Dt} = -\rho_i \mu_i (\nabla \cdot v) - \mu_i (\nabla \cdot j_i) + r_i \mu_i \quad (16)$$

With standard relationships for derivatives of products, and by summing over all species i , substituting the overall equation of continuity (Eq. (13)), and dividing through by the density, ρ , Eq. (16) becomes

$$\begin{aligned} \frac{D}{Dt} (\hat{G}) = & -\frac{1}{\rho_i} \sum_i (\nabla \cdot \mu_i j_i) + \sum_i \Omega_i \frac{D\mu_i}{Dt} \\ & + \frac{1}{\rho} \sum_i (j_i \cdot \nabla \mu_i) + \frac{1}{\rho} \sum_i r_i \mu_i \quad (17) \end{aligned}$$

The terms on the right-hand side of Eq. (17) are not all independent inasmuch as (Bird et al., 1960)

$$\sum_i j_i = j_1 + j_2 + \dots + j_n = 0 \quad (18)$$

and:

$$r_i = \sum_{j=1}^m \nu_{ij} R_j \quad (19)$$

where j_i represents the mass diffusion flux of species i . The

subscript $j = 1, 2, \dots, m$ (in Eq. (19)) represents independent chemical reactions, ν_{ij} is the stoichiometric coefficient for species i in reaction j , and R_j is the volume rate of reaction j . With these relationships, Eq. (17) may be written as

$$\frac{D}{Dt} (\hat{G}) = -\frac{1}{\rho} \sum_i (\nabla \cdot \mu_{ji}) + \sum_i \Omega_i \frac{D\mu_i}{Dt} + \frac{1}{\rho} \left[\sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) - \sum_j \lambda_j R_j \right] \quad (20)$$

where $\lambda_j \equiv -\sum_i \nu_{ij} \mu_i$ is the chemical affinity of reaction j (Prigogine and Defay, 1954). Equation (20) is the desired equation of chemical energy. This equation states that, for an element of fluid moving with the mass-average velocity, the chemical energy changes because of (i) the net transport of chemical energy by diffusion, (ii) the reversible interconversion with thermal and/or strain energy (via the Gibbs-Duhem relation), and (iii) the irreversible conversion of chemical energy to thermal energy (a) versus diffusion and (b) via chemical reactions.

The Composite Equation of Energy

The equation of kinetic energy (Eq. (3)), the equation of thermal energy (Eq. (12)), the equation of strain energy (Eq. (15)), and the equation of chemical energy (Eq. (20)) are the component equations of energy. As shown presently, the sum of these four equations is indeed equivalent to the equation of energy (Eq. (1))

$$\begin{aligned} \frac{D}{Dt} (\hat{E}) = & \left[-\frac{1}{\rho} (\nabla \cdot [\tau_s \cdot v]) + \frac{1}{\rho} (\tau_s : \nabla v) \right. \\ & \quad (i) \quad (ii) \\ & -\frac{1}{\rho} (v \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} \sum_i (n_i \cdot g_i) - \frac{1}{\rho} \sum_i (j_i \cdot g_i) \\ & \quad (iii) \quad (iv) \quad (v) \\ & + \left[-\frac{1}{\rho} (\nabla \cdot T\sigma) + \hat{S} \frac{DT}{Dt} - \frac{1}{\rho} (\tau_s : \nabla v) \right. \\ & \quad (vi) \quad (vii) \quad (viii) \\ & -\frac{1}{\rho} (\tau_n : \nabla v) - \frac{1}{\rho} \sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) \\ & \quad (ix) \quad (x) \\ & + \frac{1}{\rho} \sum_j \lambda_j R_j + \frac{1}{\rho} \sum_i (j_i \cdot g_i) \\ & \quad (xi) \quad (xii) \\ & + \left[-\frac{1}{\rho} (\nabla \cdot [\pi_n \cdot v]) - v \frac{DP}{Dt} \right. \\ & \quad (xiii) \quad (xiv) \\ & + \frac{1}{\rho} (v \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} (\tau_n : \nabla v) \\ & \quad (xv) \quad (xvi) \\ & + \left[-\frac{1}{\rho} \sum_i (\nabla \cdot \mu_{ji}) + \sum_i \Omega_i \frac{D\mu_i}{Dt} \right. \\ & \quad (xvii) \quad (xviii) \\ & + \frac{1}{\rho} \sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) - \frac{1}{\rho} \sum_j \lambda_j R_j \\ & \quad (xix) \quad (xx) \end{aligned} \quad (21)$$

Equation (21) is the equation of energy in which all the energy interconversions and transports are explicitly shown. The first set of brackets contains the changes of kinetic energy, the second set the changes of thermal energy, the third set the changes of strain energy, and the last set the changes of chemical energy. By (i) canceling all like terms, (ii) employing the

Gibbs-Duhem relation, (iii) incorporating the relation $q = T\sigma + \sum \mu_j j_j$, and (iv) employing the relation (for inelastic fluids), $\pi = \pi_n + \tau_s$, Eq. (21) reduces to a familiar form of the equation of energy (e.g., Eq. (1)).

Along with the Gibbs-Duhem relation (Eq. (6)) and the expression for the local rate of entropy production (Eq. (7)), the equation of energy in the form of Eq. (21) allows for the justification of the previous interpretations of the terms describing energy transports and interconversions. The following is a term-by-term interpretation of the twenty terms shown on the right-hand side of Eq. (21).

There are five energy transport terms. Term (i) represents the net transport of kinetic energy via shear stresses; term (iv) the net transport of kinetic energy via the work done on the fluid by body forces; term (vi) the net transport of thermal energy via diffusion and heat transfer; term (xiii) the net transport of strain energy via normal stresses, and term (xvii) the net transport of chemical energy via diffusion.

In addition, there are a number of energy interconversions which are deemed reversible since the terms representing such conversions do not appear in the expression for the local rate of entropy production (Eq. (7)). For example, terms (iii) and (xv) represent the reversible interconversion between kinetic and strain energy, these terms being the same but of opposite sign in the respective equations of change. Terms (vii), (xiv) and (xviii) signify the reversible interconversions between thermal, strain and chemical energy, inasmuch as these Stokes time derivative terms are subject to the Gibbs-Duhem relation (Eq. (6)), rewritten here on a Stokes time derivative basis

$$\hat{S} \frac{DT}{Dt} - v \frac{DP}{Dt} + \sum_i \Omega_i \frac{D\mu_i}{Dt} = 0 \quad (22)$$

The reversible interconversions of Eq. (22) are dependent on the property relations of the material.

Finally, there are terms which are justifiably considered as irreversible conversions of energy inasmuch as these terms also appear in the equation of entropy production (Eq. (7)). Terms (ii) and (viii) stand for the irreversible conversion of kinetic energy to thermal energy via shear stresses. Terms (v) and (xii) represent the irreversible conversion of gravitational energy (and that associated with other body forces) to thermal energy via diffusion. (Term (iv) represents the net mechanical transfer of energy via work done on the fluid by body forces. The net effect of terms (iv) and (v) signifies the net transfer of kinetic energy via the work done on the fluid by body forces (see Eq. (3)).)

Terms (ix) and (xvi) represent the irreversible conversion of strain energy to thermal energy via normal stresses. Finally, terms (x) and (xix) signify irreversible conversion of chemical energy to thermal energy via diffusion; terms (xi) and (xx) that due to chemical reactions.

Thus, all the dissipative energy conversions which contribute to the local rate of entropy production (see Eq. (7)) appear in Eq. (21), except the term $(\sigma \cdot \nabla T)$. This occurs because $\sigma \cdot \nabla T$ is a degradation of thermal energy but does not change the amount of thermal energy. Hence, this term would only appear in an equation of change for thermal exergy.

The Equation of Mechanical Energy

Other equations of change may be developed by simply forming various combinations of the four component equations of energy. For example, two such resulting relations which are worthy of mention are "the equation of mechanical energy" and "the equation of thermochemical energy."

By adding the equations of kinetic energy (Eq. (3)) and strain energy (Eq. (15))

$$\frac{D}{Dt} (\hat{K} - P_v) = -\frac{1}{\rho} (\nabla \cdot [\pi \cdot v]) + \frac{1}{\rho} \sum_i (n_i \cdot g_i) - v \frac{DP}{Dt} + \frac{1}{\rho} (\tau : \nabla v) - \frac{1}{\rho} \sum_i (j_i \cdot g_i) \quad (23)$$

In this form, "the equation of mechanical energy" states that, for an element of fluid moving with the mass-average velocity, the mechanical energy changes because of (i) the net transport of mechanical energy via stresses, (ii) the net transport of mechanical energy via body forces, (iii) the reversible interconversion with thermochemical energy via the Gibbs-Duhem relation, (iv) the portion of the transport via stresses which is irreversibly converted to thermochemical energy, and (v) the portion of the transport via body forces which is irreversibly converted to thermochemical energy.

The Equation of Thermochemical Energy

By adding the equations of thermal energy (Eq. (12)) and chemical energy (Eq. (20))

$$\frac{D}{Dt} (T\hat{S} + \hat{G}) = \frac{D}{Dt} (\hat{H}) = -\frac{1}{\rho} (\nabla \cdot e) - \frac{1}{\rho} \left(\nabla \cdot \sum_i \hat{H}_{ji} \right) + \hat{S} \frac{DT}{Dt} + \sum_i \Omega_i \frac{D\mu_i}{Dt} + \frac{1}{\rho} \left[-(\tau : \nabla v) + \sum_i (j_i \cdot g_i) \right] \quad (24)$$

where $e = T\sigma - T\nabla \hat{S}_{ji}$. In this form, the equation of thermochemical energy (or the equation of enthalpy) states that, for an element of fluid moving with the mass-average velocity, the thermochemical energy changes because of (line i) the net transports of thermochemical energy by: (a) conduction and radiation and (b) diffusion, line (ii) the reversible interconversions with strain energy via the Gibbs-Duhem relation, and line (iii) irreversible conversion of mechanical energy to thermal energy.

Exergy

Attention now turns to the component equations of exergy. These differential equations complement the foregoing set of component equations of energy by (i) further justifying the categorization of reversible and irreversible energy conversions, and (ii) revealing quantitatively the amount of irreversibility associated with the various energy transformations.

The Equation of Exergy

The specific exergy is given by the relation (e.g., Moran, 1989; Szargut et al., 1988)

$$\hat{a} = \hat{K} + \hat{\Phi} + \hat{U} + P_o v - T_o \hat{S} - \sum_i \mu_{io} \Omega_i \quad (25)$$

where P_o , T_o and μ_{io} are characteristics of the reference environment and, by definition, $\hat{\Phi} = \sum \Omega_i \phi_i$ is the potential exergy of the element and its environment due to the existence of conservative body forces.

The Stokes derivative of the exergy yields

$$\frac{D\hat{a}}{Dt} = \frac{D}{Dt} (\hat{U} + \hat{K} + \hat{\Phi}) + \frac{D}{Dt} (P_o v) - \frac{D}{Dt} (T_o \hat{S}) - \frac{D}{Dt} \left(\sum_i \mu_{io} \Omega_i \right) \quad (26)$$

Given the relation $g_i = -\nabla \phi_i + f_i$ (where ϕ_i represents the potential on species i per unit matter due to any present conservative force fields and f_i is the body force on species i per unit matter due to the existence of nonconservative force fields), it follows from Eq. (1) that the Stokes derivative of the quantity $(\hat{U} + \hat{K} + \hat{\Phi})$ may be written as:

$$\frac{D}{Dt} (\hat{U} + \hat{K} + \hat{\Phi}) = -\frac{1}{\rho} (\nabla \cdot q) - \frac{1}{\rho} (\nabla \cdot [\pi \cdot v]) - \frac{1}{\rho} \sum_i (\nabla \cdot \phi_{ji}) + \frac{1}{\rho} \sum_i (n_i \cdot f_i) + \frac{1}{\rho} \sum_i \phi_i r_i \quad (27)$$

Substitution of (i) Eq. (27), (ii) the volume balance (Eq. (14)), (iii) the entropy balance (e.g., Eq. (11.1-13) of Hirschfelder et al., 1954), (iv) the equation of entropy production (Eq. (7)), and (v) the equation of continuity of the individual species (e.g., Eq. (11.1-1) of Hirschfelder et al., 1954) into Eq. (26) results in the equation of exergy

$$\begin{aligned} \frac{D\hat{a}}{Dt} = & -\frac{1}{\rho} \left(\nabla \cdot \left(1 - \frac{T_o}{T} \right) \epsilon \right) - \frac{1}{\rho} \sum_i (\nabla \cdot (B_i - (B_{io})j_i)) \\ & - \frac{1}{\rho} (\nabla \cdot [\pi - P_o \delta] \cdot v) - \frac{1}{\rho} \sum_i (\nabla \cdot \phi_{ji}) + \frac{1}{\rho} \sum_i (n_i \cdot f_i) \\ & - \frac{T_o}{\rho T} \left[-(\tau_s : \nabla v) - (\tau_n : \nabla v) - \sum_i (j_i \cdot \nabla \phi_i) \right. \\ & \left. + \sum_i (j_i \cdot f_i) - \sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) - (\sigma \cdot \nabla T) + \sum_j \lambda_j R_j \right] \\ & + \left[v \frac{DP_o}{Dt} - \hat{S} \frac{DT_o}{Dt} - \sum_i \Omega_i \frac{D\mu_{io}}{Dt} \right] \\ & + \frac{1}{\rho} \sum_i \phi_i r_i - \frac{1}{\rho} \sum_i \mu_{io} r_i \quad (28) \end{aligned}$$

In this form, the equation of exergy states that, for an element of fluid moving with the mass-average velocity, the exergy changes because of (i) the net transport of exergy via thermal conduction and radiation, (ii) the net transport of exergy by diffusion, (iii) the net mechanical transport of exergy from surrounding fluid elements via stresses, (iv) the net transfer of potential exergy by diffusion, (v) the net mechanical transfer of exergy from remote material via nonconservative body forces, (vi) the net destruction of exergy associated with (a) conversion of kinetic energy to thermal energy, (b) conversion of strain energy to thermal energy, (c) conversion of potential exergy to thermal energy, (d) conversion of mechanical energy, transmitted via nonconservative body forces, to thermal energy, (e) conversion of chemical energy to thermal energy by diffusion, (f) degradation of thermal energy via the heat flux, and (g) conversion of chemical energy to thermal energy by reactions, (vii) any changes of the intensive properties of the reference environment, and (viii) changes in potential exergy due to reactions. Although term (ix) could be nonzero (Gaggioli and El-Sayed, 1989), it is typically zero insofar as the terms in this summation cancel each other (as long as there has been no redundancy in the selection of the environmental components; e.g., the number of selected environmental components is equal to the number of elements independently involved in reactions). Equation (28) generalizes that of Gaggioli (1961).

The Decomposition of Exergy

Just as energy and the energy balance have been decomposed, the exergy is presently broken down into its component parts. By substituting Eq. (5) into Eq. (25), exergy may be expressed

$$\hat{a} = \hat{K} + \hat{\Phi} + (T - T_o) \hat{S} - (P - P_o) v + \sum_i (\mu_i - \mu_{io}) \Omega_i \quad (29)$$

Following Gaggioli and El-Sayed (1989) the terms on the right-hand side of Eq. (29) are called the kinetic, potential, thermal, strain, and chemical exergy, respectively. The equations of change for these exergy forms are presently derived.

tion $q = T\sigma$
astic fluids),
the equation

(6) and the
on (Eq. (7)),
flows for the
he terms de-
he following
as shown on

(v) represents
es; term (iv)
done on the
of thermal
he net trans-
m (xvii) the

conversions
enting such
e local rate
ms (iii) and
een kinetic
of opposite
s (vii), (xiv)
etween ther-

Stokes time
elation (Eq.
asis

(22)

dependent on

considered as
se terms also
(7)). Terms

on of kinetic
(v) and (xii)
ional energy
ermal energy
hical transfer
rces. The net
fer of kinetic
rces (see Eq.

onversion of
ses. Finally,
of chemical
and (xx) that

h contribute
(7)) appear in
cause $\sigma \cdot \nabla T$
t change the
only appear

ed by simply
onent equa-
ng relations
f mechanical
nergy."

b)) and strain

the ASME

The Equation of Thermal Exergy

The Stokes derivative of the thermal exergy yields

$$\frac{D}{Dt} (T - T_o) \hat{S} = \frac{D}{Dt} (T \hat{S}) - T_o \frac{D \hat{S}}{Dt} - \hat{S} \frac{DT_o}{Dt} \quad (30)$$

Substituting the equations of thermal energy (Eq. (12)) and entropy (e.g., Eq. (11.1-13) of Hirschfelder et al., 1954) into this equation results in

$$\begin{aligned} \frac{D}{Dt} (T - T_o) \hat{S} = & -\frac{1}{\rho} (\nabla \cdot T \sigma) + \hat{S} \frac{DT}{Dt} \\ & + \frac{1}{\rho} \left[-(\tau_s : \nabla v) - (\tau_n : \nabla v) - \sum_i (j_i \nabla (\mu_i - \mu_n)) \right. \\ & \left. + \sum_j \lambda_j R_j + \sum_i (j_i \cdot g_i) \right] - \frac{T_o}{\rho} [(\nabla \cdot \sigma) + g] - \hat{S} \frac{DT_o}{Dt} \quad (31) \end{aligned}$$

Further substitution of the expression for the volumetric rate of irreversible entropy production (Eq. (7)) and the relation $g_i = -\nabla \phi_i + f_i$ results in the equation of thermal exergy

$$\begin{aligned} \frac{D}{Dt} (T - T_o) \hat{S} = & -\frac{1}{\rho} (\nabla \cdot (T - T_o) \sigma) + \hat{S} \frac{DT}{Dt} + \frac{T_o}{\rho T} (\sigma \cdot \nabla T) \\ & + \frac{1}{\rho} \left(1 - \frac{T_o}{T} \right) \left[\left\{ -(\tau_s : \nabla v) - (\tau_n : \nabla v) - \sum_i (j_i \cdot \nabla \phi_i) \right. \right. \\ & \left. \left. + \sum_i (j_i \cdot f_i) \right\} + \left\{ \sum_j \lambda_j R_j - \sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) \right\} \right] - \hat{S} \frac{DT_o}{Dt} \quad (32) \end{aligned}$$

In this form, the equation of thermal exergy states that, for an element of fluid moving with the mass-average velocity, the thermal exergy changes because of (i) the net transport of thermal exergy via diffusion, conduction and radiation, (ii) the reversible interconversion(s) with strain and/or chemical exergy, (iii) the irreversible decrease in thermal exergy with the entropy flux, (iv) the thermal exergy gain due to the irreversible conversion of mechanical and chemical energy to thermal energy (see Eqs. (12), (20), and (23)), and (v) any change in the temperature of the reference environment.

The Equation of Strain Exergy

By taking the Stokes derivative of the strain exergy and substituting Eqs. (14) and (15)

$$\begin{aligned} \frac{D}{Dt} (-(P - P_o)v) = & \frac{D}{Dt} (-Pv) + P_o \frac{Dv}{Dt} + v \frac{DP_o}{Dt} \\ = & -\frac{1}{\rho} (\nabla \cdot [\pi_n - P_o \delta] \cdot v) - v \frac{DP}{Dt} \\ & + \frac{1}{\rho} (\nu \cdot [\nabla \cdot \pi_n]) + v \frac{DP_o}{Dt} + \frac{1}{\rho} (\tau_n : \nabla v) \quad (33) \end{aligned}$$

This equation of strain exergy states that, for an element of fluid moving with the mass-average velocity, the strain exergy changes because of (i) the net transport of strain exergy via normal stresses, (ii) the reversible interconversion(s) with thermal and/or chemical exergy, (iii) the net reversible interconversion with kinetic exergy, (iv) any change in the pressure of the environment, and (v) the irreversible decrease in strain exergy due to the conversion of strain energy to thermal energy. The fraction $(1 - T_o/T)$ of this irreversible decrease is converted to thermal exergy (see Eq. (32)) and the fraction (T_o/T) is destroyed (see Eq. (28)).

The Equation of Chemical Exergy

By taking the Stokes derivative of the chemical exergy and substituting the equation of continuity of the individual species (e.g., Eq. (11.1-1) of Hirschfelder et al., 1954) and Eq. (20)

$$\begin{aligned} \frac{D}{Dt} \sum_i (\mu_i - \mu_{io}) \Omega_i = & \frac{D}{Dt} \sum_i \Omega_i \mu_i - \sum_i \mu_{io} \frac{D \Omega_i}{Dt} \\ & - \sum_i \Omega_i \frac{D \mu_{io}}{Dt} = -\frac{1}{\rho} \sum_i (\nabla \cdot \mu_{ji}) + \sum_i \Omega_i \frac{D \mu_i}{Dt} \\ & + \frac{1}{\rho} \left[\sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) - \sum_j \lambda_j R_j \right] \\ & - \frac{1}{\rho} \sum_i \mu_{io} [-(\nabla \cdot j_i) + r_i] - \sum_i \Omega_i \frac{D \mu_{io}}{Dt} \quad (34) \end{aligned}$$

Rearranging and, in accord with the earlier discussion, setting $\sum \mu_{io} r_i$ equal to zero results in the equation of chemical exergy

$$\begin{aligned} \frac{D}{Dt} \sum_i (\mu_i - \mu_{io}) \Omega_i = & -\frac{1}{\rho} \sum_i (\nabla \cdot (\mu_i - \mu_{io}) j_i) + \sum_i \Omega_i \frac{D \mu_i}{Dt} \\ & + \frac{1}{\rho} \left[\sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) - \sum_j \lambda_j R_j \right] - \sum_i \Omega_i \frac{D \mu_{io}}{Dt} \quad (35) \end{aligned}$$

In this form, the equation of chemical exergy states that, for an element of fluid moving with the mass-average velocity, the chemical exergy changes because of (i) the net transport of chemical exergy by diffusion, (ii) the reversible interconversion(s) with thermal and/or strain exergy, (iii) the dissipative conversion of chemical energy to thermal energy of which the fraction $(1 - T_o/T)$ becomes thermal exergy (see Eq. (32)) and the fraction (T_o/T) is destroyed (see Eq. (28)), and (iv) any changes in the reference chemical potentials.

The Equation of Internal Exergy

In analogy to the equation of internal energy, an equation of internal exergy is now developed. By adding Eqs. (32), (33) and (35), collecting terms, and employing the Gibbs-Duhem relation, a form of the equation of internal exergy results

$$\begin{aligned} \frac{D}{Dt} \hat{a}_I = & \frac{D}{Dt} (T - T_o) \hat{S} + \frac{D}{Dt} (-(P - P_o)v) + \frac{D}{Dt} \sum_i (\mu_i - \mu_{io}) \Omega_i \\ = & -\frac{1}{\rho} (\nabla \cdot (T - T_o) \sigma) - \frac{1}{\rho} (\nabla \cdot (\pi_n - P_o \delta) \cdot v) \\ & - \frac{1}{\rho} \sum_i (\nabla \cdot (\mu_i - \mu_{io}) j_i) + \frac{1}{\rho} (\nu \cdot [\nabla \cdot \pi_n]) \\ & + \frac{1}{\rho} \left(1 - \frac{T_o}{T} \right) [-(\tau_s : \nabla v) - \sum_i (j_i \cdot \nabla \phi_i) + \sum_i (j_i \cdot f_i)] \\ & - \frac{1}{\rho} \left(\frac{T_o}{T} \right) [-(\tau_n : \nabla v) - \sum_i (j_i \cdot \nabla (\mu_i - \mu_n))] \\ & + \sum_j \lambda_j R_j - (\sigma \cdot \nabla T) + \left[v \frac{DP_o}{Dt} - \hat{S} \frac{DT_o}{Dt} - \sum_i \Omega_i \frac{D \mu_{io}}{Dt} \right] \quad (36) \end{aligned}$$

Another form is obtained by substituting the relations $\sigma = \epsilon/T + \Sigma \hat{S}_j j_i$ and $B_i = \hat{H}_i - T_o \hat{S}_i$ into Eq. (36)

energy and
equal species
and Eq. (20)

$$\begin{aligned} \frac{D}{Dt} \hat{a}_I = & -\frac{1}{\rho} \left(\nabla \cdot \left(1 - \frac{T_o}{T} \right) \epsilon \right) - \frac{1}{\rho} \sum_i (\nabla \cdot (B_i - B_{io}) j_i) \\ & - \frac{1}{\rho} (\nabla \cdot (\pi_n - P_o \delta) \cdot \nu) + \frac{1}{\rho} (\nu \cdot [\nabla \cdot \pi_n]) \\ & + \frac{1}{\rho} \left(1 - \frac{T_o}{T} \right) [-(\tau_s : \nabla \nu) - \sum_i (j_i \cdot \nabla \phi_i) + \sum_i (j_i \cdot f_i)] \\ & - \frac{1}{\rho} \left(\frac{T_o}{T} \right) [-(\sigma \cdot \nabla T) - (\tau_n : \nabla \nu) - \sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) \\ & + \sum_j \lambda_j R_j] + \left[v \frac{DP_o}{Dt} - S \frac{DT_o}{Dt} - \sum_i \Omega_i \frac{D\mu_{io}}{Dt} \right] \quad (37) \end{aligned}$$

This equation states that, for an element of fluid moving with the mass-average velocity, the internal exergy changes because of (i) the net transport of exergy via thermal conduction and radiation, (ii) the net transport of exergy via diffusion, (iii) the net transport of exergy via normal stresses, (iv) the nondissipative interconversion between kinetic and strain exergy, (v) the internal exergy increase due to the irreversible conversion of kinetic and potential exergy (see Eq. (38)), (vi) the destruction of exergy associated with (a) the entropy flux, and the irreversible conversion(s) of (b) strain energy to thermal energy, (c) chemical energy to thermal energy via diffusion, and (d) chemical energy to thermal energy via reactions, and (vii) any changes in the intensive properties of the reference environment.

The Equation of Kinetic and Potential Exergy

By subtracting Eq. (37) from Eq. (28), the equation of kinetic and potential exergy results

$$\begin{aligned} \frac{D}{Dt} (\hat{K} + \hat{\Phi}) = & -\frac{1}{\rho} (\nabla \cdot [\tau_s \cdot \nu]) - \frac{1}{\rho} \sum_i (\nabla \cdot \phi_{ji}) + \frac{1}{\rho} \sum_i (n_i \cdot f_i) \\ & - \frac{1}{\rho} (\nu \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} \sum_i \phi_i r_i \\ & + \frac{1}{\rho} (\tau_s : \nabla \nu) + \frac{1}{\rho} \sum_i (j_i \cdot \nabla \phi_i) - \frac{1}{\rho} \sum_i (j_i \cdot f_i) \quad (38) \end{aligned}$$

This equation states that, for an element of fluid moving with the mass-average velocity, the kinetic and potential exergy changes because of (i) the net transport of kinetic exergy via shear stresses, (ii) the net transport of potential exergy via diffusion, (iii) the net mechanical transport of exergy via work done on the fluid by nonconservative body forces, (iv) the net reversible interconversion with strain exergy, (v) potential exergy changes as a consequence of chemical reactions, (vi) the irreversible conversion of kinetic energy to thermal energy via shear stresses, (vii) the irreversible conversion of potential exergy to thermal energy, and (viii) the portion of the transport via nonconservative body forces which is irreversibly converted to thermal energy. The fraction $(1 - T_o/T)$ of these irreversible conversions becomes thermal exergy (Eq. (32)); the fraction (T_o/T) is destroyed (Eq. (28)).

The Equation of Potential Exergy

By subtracting Eq. (3) from Eq. (38), the equation of potential exergy results

$$\frac{D\hat{\Phi}}{Dt} = -\frac{1}{\rho} \sum_i (\nabla \cdot \phi_{ji}) + \frac{1}{\rho} \sum_i (n_i \cdot \nabla \phi_i) + \frac{1}{\rho} \sum_i \phi_i r_i \quad (39)$$

This equation states that, for an element of fluid moving with the mass-average velocity, the potential exergy changes because of (i) the net transport of potential exergy via diffusion, (ii) the interconversion between kinetic and potential exergy,

and (iii) the potential exergy changes as a consequence of reactions.

The Composite Equation of Exergy

The equation of kinetic exergy (Eq. (3)), the equation of potential exergy (Eq. (39)), the equation of thermal exergy (Eq. (32)), the equation of strain exergy (Eq. (33)), and the equation of chemical exergy (Eq. (35)) are the component equations of exergy. The sum of these five equations is

$$\begin{aligned} \frac{D}{Dt} \hat{a} = & \left\{ -\frac{1}{\rho} (\nabla \cdot [\tau_s \cdot \nu]) + \frac{1}{\rho} \sum_i (n_i \cdot f_i) - \frac{1}{\rho} \sum_i (n_i \cdot \nabla \phi_i) \right. \\ & \quad (i) \quad (ii) \quad (iii) \\ & - \frac{1}{\rho} (\nu \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} (\tau_s : \nabla \nu) - \frac{1}{\rho} \sum_i (j_i \cdot f_i) \\ & \quad (iv) \quad (v) \quad (vi) \\ & \left. + \frac{1}{\rho} \sum_i (j_i \cdot \nabla \phi_i) \right\} \\ & \quad (vii) \\ & + \left\{ -\frac{1}{\rho} \sum_i (\nabla \cdot \phi_{ji}) + \frac{1}{\rho} \sum_i (n_i \cdot \nabla \phi_i) + \frac{1}{\rho} \sum_i \phi_i r_i \right\} \\ & \quad (viii) \quad (ix) \quad (x) \\ & + \left\{ -\frac{1}{\rho} (\nabla \cdot (T - T_o) \sigma) + S \frac{DT}{Dt} + \frac{T_o}{\rho T} (\sigma \cdot \nabla T) \right. \\ & \quad (xi) \quad (xii) \quad (xiii) \\ & \left. + \frac{1}{\rho} \left(1 - \frac{T_o}{T} \right) [-(\tau_s : \nabla \nu) - (\tau_n : \nabla \nu) - \sum_i (j_i \cdot \nabla \phi_i) \right. \\ & \quad (xiv) \quad (xv) \quad (xvi) \\ & \left. + \sum_i (j_i \cdot f_i) + \sum_j \lambda_j R_j - \sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) \right. \\ & \quad (xvii) \quad (xviii) \quad (xix) \\ & \left. - S \frac{DT_o}{Dt} \right\} \\ & \quad (xx) \\ & + \left\{ -\frac{1}{\rho} (\nabla \cdot [\pi_n - P_o \delta] \cdot \nu) - v \frac{DP}{Dt} \right. \\ & \quad (xxi) \quad (xxii) \\ & \left. + \frac{1}{\rho} (\nu \cdot [\nabla \cdot \pi_n]) + \frac{1}{\rho} (\tau_n : \nabla \nu) + v \frac{DP_o}{Dt} \right\} \\ & \quad (xxiii) \quad (xxiv) \quad (xxv) \\ & + \left\{ -\frac{1}{\rho} \sum_i (\nabla \cdot (\mu_i - \mu_{io}) j_i) + \sum_i \Omega_i \frac{D\mu_i}{Dt} \right. \\ & \quad (xxvi) \quad (xxvii) \\ & \left. + \frac{1}{\rho} \left[\sum_i (j_i \cdot \nabla (\mu_i - \mu_n)) - \sum_j \lambda_j R_j \right] \right. \\ & \quad (xxviii) \quad (xxix) \\ & \left. - \sum_i \Omega_i \frac{D\mu_{io}}{Dt} \right\} \quad (40) \\ & \quad (xxx) \end{aligned}$$

Equation (40) is a form of the equation of exergy in which all the exergy interconversions, transports, and destructions are explicitly shown. The first set of brackets contains the changes of kinetic exergy, the second set the changes of potential exergy, the third set the changes of thermal exergy, the fourth set the changes of strain exergy, and the last set the changes of chemical exergy. By (i) canceling all like terms, (ii) employing the Gibbs-Duhem relation (Eq. (22)), (iii) incor-

$\frac{D\mu_i}{Dt}$ (34)

tion, set-
chemical

$\frac{D\mu_i}{Dt}$ (35)

states that,
the velocity,
transport
intercon-
dissipative
which the
(32) and
(iv) any

equation
(32), (33)
Gibbs-Duhem
results

$\mu_{io} \Omega_i$

$j_i \cdot f_i$

$\Omega_i \frac{D\mu_{io}}{Dt}$ (36)

itions $\sigma =$

ASME

porating the relationships $\sigma = \epsilon/T + \sum \hat{S}_j$ and $B_i = H_i - T_o S_i$, and employing the relation (for inelastic fluids) $\pi = \tau_s + \pi_n$, Eq. (40) reduces to a form of the equation of exergy (e.g., Eq. (28)). The following is a term-by-term interpretation of the thirty terms shown on the right-hand side of Eq. (40).

There are six transport terms: Term (i) represents the net transport of kinetic exergy via shear stresses; term (ii) the net transport of kinetic exergy via the work done by nonconservative body forces; term (viii) the net transport of potential exergy via diffusion; term (xi) the net transport of thermal exergy via diffusion, conduction and radiation; term (xxi) the net transport of strain exergy via normal stresses, term (xxvii) the net transport of chemical exergy via diffusion.

There are a number of exergy interconversions which are deemed reversible since the full amount of exergy converted appears as another type of exergy, none being destroyed. For example, terms (iv) and (xxiii) represent a reversible interconversion between kinetic and strain exergy. Terms (xii), (xxii), and (xxvii) are reversible interconversions between thermal, strain, and chemical exergy, subject to the Gibbs-Duhem relation. Finally, terms (iii) and (ix) represent reversible interconversion between kinetic and potential exergy.

Terms (xx), (xxv) and (xxx) are changes of exergy due to changes in the intensive properties of the reference environment. Term (x) is a change in exergy as a consequence of the potential exergy change associated with reactions. Each of these exergy changes may go in either direction and thus, these terms may be positive or negative in value.

The remaining terms represent irreversible conversions of exergy. For example, term (v) is the irreversible conversion of kinetic exergy of which the fraction $(1 - T_o/T)$ becomes thermal exergy (term (xiv)); the fraction (T_o/T) is destroyed. Term (vi) is the portion of the exergy transport via nonconservative body forces which is irreversibly converted to thermal energy, and term (xvii) is the fraction which becomes thermal exergy. Term (vii) is the portion of the potential to kinetic exergy conversion (terms (ix) and (iii)) which is irreversibly converted to thermal energy, and term (xvi) is the fraction which becomes thermal exergy.

Term (xxiv) is the irreversible conversion of strain exergy of which the fraction $(1 - T_o/T)$ becomes thermal exergy (term (xv)), the fraction (T_o/T) is destroyed. Similar logic holds for terms (xxviii) and (xxix) which represent the irreversible conversions of chemical to thermal exergy (a) by diffusion and (b) via chemical reactions, respectively. Finally, term (xiii) is the destruction of exergy as a consequence of entropy flow in the direction of lower temperatures.

The Equation of Mechanical Exergy

By adding Eqs. (33) and (38)

$$\begin{aligned} \frac{D}{Dt} (\hat{K} + \Phi - (P - P_o)v) = & -\frac{1}{\rho} (\nabla \cdot (\pi - P_o \delta) \cdot v) \\ & - \frac{1}{\rho} \sum_i (\nabla \cdot \phi_j i) + \frac{1}{\rho} \sum_i (n_i \cdot f_i) - v \frac{DP}{Dt} + \frac{1}{\rho} \sum_i \phi_i \dot{r}_i + v \frac{DP_o}{Dt} \\ & + \frac{1}{\rho} [(\tau_n \cdot \nabla v) + (\tau_s \cdot \nabla v) + \sum_i (j_i \cdot \nabla \phi_i) - \sum_i (j_i \cdot f_i)] \quad (41) \end{aligned}$$

This equation of mechanical exergy states that, for an element of fluid moving with the mass-average velocity, the mechanical exergy changes because of (i) the net transport of mechanical exergy via stresses, (ii) the net transport of potential exergy via diffusion, (iii) the net transport of exergy via work done on the fluid by nonconservative body forces, (iv) the reversible interconversion(s) with thermal and/or chemical exergy, (v) the potential exergy change as a consequence of reactions, (vi) any changes in the reference pressure, and (vii) the dissipation of mechanical exergy of which the fraction

$(1 - T_o/T)$ becomes thermal exergy and the fraction (T_o/T) is destroyed.

The Equation of Thermochemical Exergy

By adding the Eqs. (32) and (35)

$$\begin{aligned} \frac{D}{Dt} [(T - T_o)\hat{S} + \sum_i (\mu_i - \mu_{io})\Omega_i] = & \frac{D}{Dt} [\hat{H} - T_o\hat{S} - \sum_i \mu_{io}\Omega_i] \\ = & -\frac{1}{\rho} [(\nabla \cdot (T - T_o)\sigma) - \sum_i (\nabla \cdot (\mu_i - \mu_{io})j_i)] \\ & + \left[\hat{S} \frac{DT}{Dt} + \sum_i \Omega_i \frac{D\mu_i}{Dt} \right] + \frac{T_o}{\rho T} [(\sigma \cdot \nabla T) \\ & + \sum_i (j_i \nabla (\mu_i - \mu_n)) - \sum_j \lambda_j R_j] + \frac{1}{\rho} \left(1 - \frac{T_o}{T} \right) [-(\tau_s \cdot \nabla v) \\ & - (\tau_n \cdot \nabla v) - \sum_i (j_i \cdot \nabla \phi_i) + \sum_i (j_i \cdot f_i)] \\ & - \left[\hat{S} \frac{DT_o}{Dt} + \sum_i \Omega_i \frac{D\mu_{io}}{Dt} \right] \quad (42) \end{aligned}$$

This equation of thermochemical exergy states that, for an element of fluid moving with the mass-average velocity, the thermochemical exergy changes because of (i) the net transport of thermochemical exergy (a) with the entropy flux, and (b) by diffusion, (ii) the reversible interconversion with strain exergy, (iii) the decrease in thermochemical exergy (a) with the irreversible heat flux, (b) by diffusion, and (c) via chemical reactions, (iv) the thermal exergy increase due to the irreversible conversion of mechanical exergy, and (v) any changes in the reference chemical potentials and/or temperature.

Closure

In this work, definitions for thermal, strain, and chemical energy/exergy as well as mechanical and thermochemical energy/exergy are derived, and the equations of change for these properties are presented. The resulting equations explicitly contain (a) the breakdown of each energy/exergy transport and interconversion into component parts, and (b) terms which describe the reversible and irreversible conversions of energy. The sum of these component equation of energy/exergy results in equations of energy/exergy that contain interconversion terms which are absent from the traditional forms of the equations of energy/exergy. The transport and interconversion terms allow for a deeper understanding of the various processes.

Acknowledgments

The support of the University of Pennsylvania and of the Society of Automotive Engineers to one of the authors (WRD) is gratefully acknowledged.

References

- Bird, R. B., Stewart, W. E., and Lightfoot, E. N., 1960, *Transport Phenomena*. John Wiley and Sons, Inc., New York.
- Bird, R. B., "The Equations of Change and the Macroscopic Mass, Momentum, and Energy Balances," *Chemical Engineering Science*, Vol. 6, pp. 123-131.
- DeGroot, S. R., and Mazur, P., 1962, *Nonequilibrium Thermodynamics*, North Holland Publishing Co., New York.
- Denbigh, K. G., 1956, "The Second Law Efficiency of Chemical Processes," *Chemical Engineering Science*, Vol. 6, pp. 1-9.
- Denbigh, K. G., 1966, *The Principles of Chemical Equilibrium*, Cambridge University Press, Cambridge.
- Fan, L. T., and Shieh, J. H., 1980, "Thermodynamically-Based Analysis and Synthesis of Process Systems," *Energy*, Vol. 5, p. 955.
- Gaggioli, R. A., and El-Sayed, Y. M., 1989, "A Critical Review of Second Law Costing Methods II: Calculus Principles," *ASME JOURNAL OF ENERGY RESOURCES TECHNOLOGY*, Vol. 111, pp. 8-15.

Gaggioli
Gibbs
Green
Gyftos
Applied
Hirsch
of Gas
Ishida
Chemical
Directed
vice, V
Liu,
Process
Mah,
Second
Journal

F
PD
C
Ed
Co
inc
nu
19
\$8
To
or

- Gaggioli, R. A., 1961, "The Concept of Available Energy," *Chemical Engineering Science*, Vol. 16, pp. 87-96.
- Gibbs, J. W., 1875, *The Collected Works of J. Willard Gibbs*, Longmans, Green and Co., New York; also, Dover, New York, 1961, pp. 33-54.
- Gyftopoulos, E. P., and Beretta, G. P., *Thermodynamics: Foundations and Applications*, Macmillan, New York, 1991.
- Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., 1954, *Molecular Theory of Gases and Liquids*, Chap. 11, John Wiley and Sons, Inc., New York.
- Ishida, M., and Kawamura, K., 1982, "Energy and Exergy Analysis of a Chemical Process System with Distributed Parameters Based on the Enthalpy-Directed Factor Diagram," *Industrial Engineering Chemical Process Des. Device*, Vol. 21, p. 690.
- Liu, Y. A., Pehler, F. A., and Cahela, D. R., 1983, "Studies in Chemical Process Design and Synthesis," *AIChE Journal*.
- Mah, R. S. H., Nicholas, J. J., and Wodnik, R. B., 1977, "Distillation with Secondary Reflux and Vaporization: A Comparative Evaluation," *AIChE Journal*, Vol. 23, p. 651.
- Maxwell, J. C., 1872, *Theory of Heat*, D. Appleton and Co., New York, pp. 183-188.
- Moran, M. J., 1989, *Availability Analysis—A Guide to Efficient Energy Use*, ASME Press, New York.
- Naka, Y., Terashita, M., and Takamatsu, T., 1982, "Thermodynamic Approach to Multicomponent Distillation System Synthesis," *AIChE Journal*, Vol. 28, p. 812.
- Obert, E. F., 1960, *Concepts of Thermodynamics*, McGraw-Hill Book Company, New York.
- Prigogine, L., and Defay, R., 1954, *Chemical Thermodynamics*, Longmans and Green and Company, London.
- Szargut, J., Morris, D. R., and Steward, F. R., 1988, *Exergy Analysis of Thermal, Chemical, and Metallurgical Processes*, Hemisphere Publishing Corp., New York.
- Tsatsaronis, G., and Winhold, M., 1985, *Energy*, Vol. 10, pp. 69-64.
- Umeda, T., Niida, K., and Shiroko, K., 1979, "A Thermodynamic Approach to Heat Integration in Distillation Systems," *AIChE Journal*, Vol. 25, p. 423.

For Your ASME Bookshelf

PD-Vol. 45

Composite Material Technology — 1992

Editors: D. Hui, T. J. Kozik, and O. O. Ochoa

Composite materials are often termed the material of the future. The areas addressed in this volume include dynamics and experimental mechanics, material characterization, damage and failure, numerical analysis, and mechanics and applications.

1992 Order No. G00653 261 pp. ISBN No. 0-7918-0759-2
\$86 List / \$43 ASME Members

To order write ASME Order Department, 22 Law Drive, Box 2300, Fairfield, NJ 07007-2300 or call 800-THE-ASME (843-2763) or fax 201-882-1717.

(T_0/T) is

$[\mu_{io}]$

)]

$(\tau_s; \nabla v)$

$\left[\frac{d\mu_{io}}{dt} \right]$ (42)

at, for an
velocity, the
transport
ax, and (b)
strain ex-
with the
chemical
irreversible
changes in the

chemical
chemical en-
change for
explicitly
transport
terms which
of energy.
ergy results
conversion
n(s) of the
conversion
rious proc-

and of the
prs (WRD)

port Phenom-
ic Mass, Mo-
ol. 6, pp. 123-
modynamics,
al Processes,"

n, Cambridge
Analysis and
ew of Second
LL OF ENERGY

the ASME