THERMODYNAMIC ANALYSIS
OF PROCESS SYSTEMS

by

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CHAPTER 1

INTRODUCTION

INTRODUCTION

Because of ever increasing fuel prices and ever decreasing avail-
ability of energy resources, it is important that any industrial process
or system be developed, designed or operated in an energy efficient
manner. Thermodynamic system analysis is an effective way for attaining
and promoting the goal of efficient energy utilization; it enables us
to identify the nature and sources of inefficient energy usage in
process systems, which are essential in designing and analyzing them.

One of the most important recent developments in classical thermo-
dynamics is establishment of the so-called single axiom approach, which
reconstructs logically the laws of classical thermodynamics (see, e.g.,
Hatsopoulos and Keenan, 1962, 1965; Haywood, 1980). This axiom, which
is called the law of stable equilibrium, is a statement accepted as a
truth without proof in accordance with our experience with physical
systems; this law implies the existence of irreversibility in natural
processes.

Another important development of classical thermodynamics is the
introduction of the concept of available energy involving the notions
of exergy and essergy; it naturally follows the single axiom approach.
The concept of the available energy, originated with Gibbs and Maxwell
over a century ago, has become increasingly important because of the ever
increasing emphasis on efficient utilization of energy. This concept
has been incorporated into a variety of methods and procedures for
thermodynamically evaluating process systems. (see, e.g., Keenan, 1941;
Rant, 1956; Denbigh, 1956, 1971; Szargut and Petela, 1965; Evans, 1969;

Riekert, 1974; Haywood, 1974, 1980; Gaggioli and Petit, 1977; Gaggioli, 1980; Fan and Shieh, 1980).

The overall objective of this work is to develop a comprehensive procedure for analyzing systematically a process system, based on the law of mass conservation, and the first and second laws of thermodynamics, leading to the energy and available energy balances for the system. Then, the practical applications of the procedure are illustrated with several examples in the area of energy conservation and conversion.

This thesis consists of seven chapters. The objective is stated and the contents are summarized in the present chapter. In chapter 2, the single axiom approach in thermodynamics is reviewed; thermodynamic laws and definitions which constitute the foundation of classical thermodynamics are deduced from the single axiom. Chapter 3 deals with the specification of the reference state for measuring thermodynamic properties, derivations of the governing equations for the system analysis, and definitions of the mass utilization efficiency and the thermodynamic first-law and second-law efficiencies. A counter-current heat exchanger is analyzed rigorously from the thermodynamic point of view with the result illustrated numerically in chapter 4. In chapter 5, a biomass pyrolysis system is systematically analyzed. The thermodynamic inefficiency is identified, and the system efficiencies are evaluated for several operating modes of the system. The procedure of the thermodynamic system analysis is applied to an anaerobic sludge digestion system in chapter 6. To gain deeper insight into its performance, a preliminary optimization study is also carried out. Finally, the major conclusions are summarized and recommendation for future work are made in chapter 7.

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CHAPTER 2

SINGLE AXIOM APPROACH

SINGLE AXIOM APPROACH

All the relationships of classical thermodynamics can be deduced from a single axiom called the law of stable equilibrium (see, e.g., Hatsopoulos and Keenan, 1962, 1965; Haywood, 1980). In this chapter, the law of stable equilibrium is reviewed, which is followed by the statements of the first law of thermodynamics, the state principle and the second law of thermodynamics, both deduced from it; they constitute the foundation of classical thermodynamics.

LAW OF STABLE EQUILIBRIUM

The state of stable equilibrium is defined as (Hatsopoulos and Keenan, 1965):

> A system is in a state of stable equilibrium if a finite change of state of the system cannot occur without a corresponding finite permanent change of state of its environment.

For brevity, the state of stable equilibrium is called simply a stable state.

The law of stable equilibrium is a statement of the existence of a stable state; it is enunciated by Hatsopoulos and Keenan (1965) as follows:

> A system having specified allowed states and an upper bound in volume can reach from any given state one and only one stable state and leave no net effect on its environment.

Elimination of the words "and only one" from this statement gives rise to the second law of thermodynamics. The statement of the law of stable equilibrium quoted above also provides the sufficient condition for deriving the first law of thermodynamics as will be discussed in the succeeding section.

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is a statement of the existence of a property called energy. According to Haywood (1980), it can be stated as follows:

The work is the same for all adiabatic processes between two given stable states of a system.

This statement can be derived from the law of stable equilibrium given in the preceding section. The *adiabatic process* is defined as a process involving only work interactions between the system under consideration and the environment or any one of other systems interacting with it.

To prove the statement of the first law of thermodynamics, we assume that, contrary to the statement, system A can be transformed from stable state X_1 to stable state X_2 by two adiabatic processes, A_{12} and B_{12}, involving different amounts of work input. This work interaction may be performed by lowering weights in a paddle-wheel process. We assume that adiabatic process A_{12} is carried out by lowering two weights from a given height to the stable position, while adiabatic process B_{12} is carried out by lowering one weight. Adiabatic process B_{12} can be followed by another adiabatic process through the work interaction by the second weight; it carries system A from stable state X_2 to another stable state, namely, stable state X_3. Considering a system consisting of system A and two weights, we find this combined system reach from the same initial state to the different stable states without leaving any effect on the environment. This result violates the law of stable equilibrium. Therefore, the work is the same for all adiabatic processes between two given stable states of a system (see, e.g., Hatsopoulos and Keenan, 1965; Haywood, 1980).

By virtue of the first law, the work in an adiabatic process depends on the initial and final states only; it represents the change in the value of a property of the system, called energy, which is defined as (see, e.g., Hatsopoulos and Keenan, 1965; Keenan et al., 1975; Haywood, 1980)

$$E_2 - E_1 = -W_a \qquad (1)$$

where E is the energy and W_a the work done by the system ($W_a > 0$), or the work done on the system ($W_a < 0$) in an adiabatic process transforming the system from stable state 1 to stable state 2. Therefore, the adiabatic work may be used as a measure of energy changes. For an isolated system, we have

$$W_a = 0, \qquad (2)$$

and thus, equation (1) becomes

$$(E_1)_{iso} = (E_2)_{iso} \qquad (3)$$

or

$$(\Delta E)_{iso} = 0 \text{ or } (dE)_{iso} = 0 \qquad (4)$$

These equations indicate that the energy of the isolated system remains invariant. This is the law of conservation of energy.

STATE PRINCIPLE

The state principle is derived from the uniqueness of the stable state in the law of stable equilibrium and the definition of energy; according to Hatsopoulos and Keenan (1965):

> The stable state of a system bounded by a fixed surface and subject to fields prescribed by the environment is fully determined by its energy.

A system is called a constrained system when it is bounded by a fixed surface and subject to fields prescribed by the environment, such as gravitational, electric and magnetic fields. Therefore, it is deduced from the state principle that a constrained system containing a specified quantity of energy can assume only one stable state.

Suppose that two systems are individually in the stable states. If they are not in mutual stable equilibrium, an interaction could still occur between them. Such an interaction is called a heat interaction (see, e.g., Hatsopoulos and Keenan, 1962; Keenan et al., 1975). From the state principle, the magnitude of the heat interaction, Q, during a process not involving work interactions can be expressed as the corresponding change in energy of a system, say system A, between two stable states; in other words, we have

$$Q = E_2 - E_1 \tag{5}$$

Conventionally, the heat, Q, is positive when it is transferred into system A, and it is negative when it is transferred out of it.

By combining equations (1) and (5), the energy changes in a non-adiabatic process is expressed as

$$E_2 - E_1 = Q - W \tag{6}$$

From this expression, the law of conservation of energy, equation (3) or (4), can be derived for an isolated system, for which $Q = 0$ and $W = 0$, regardless of the nature of the changes within the system.

SECOND LAW OF THERMODYNAMICS

The following statement of the second law of thermodynamics can be directly derived from the law of stable equilibrium (Hatsopoulos and Keenan, 1965):

A system having specified allowed states and an upper
bound in volume can reach from any given state a stable
state and leave no net effect on the environment.

According to this statement of the second law of thermodynamics, a system

may undergo a change of state from a non-equilibrium state to a final stable

state even if it is completely isolated from all interactions with its

environment and with any other systems. For example, we may observe that

a small ball moving around in an isolated rigid bowl (a non-equilibrium state)

settles to the bottom of it (a stable state), due to friction. From the law

of stable equilibrium, a system settled to the stable state can not depart

from it; thus, the system can not be restored to the initial state, while it

remains isolated. Therefore, the second law of thermodynamics indicates the

existence of irreversibility in natural processes, a measure of which is

called the entropy of a system (see, e.g., Hatsopoulos and Keenan, 1965;

Haywood, 1980).

Although the foregoing statement of the second-law of thermodynamics is

an unfamiliar one, the familiar statements can be deduced from it. For

example, let us consider system A which is initially at stable state 1 with

energy E_1; then, it may be transformed from stable state 1 to stable state 2

with energy E_2 by both the work and heat interactions with the work sink and

heat source (reservoir), respectively. The heat source is considered a

constrained system initially in a stable state (SS_1). Therefore, from equation

(6), we have

$$E_2 - E_1 = Q - W \qquad\qquad (7)$$

If we assume that the heat transferred to system A could be completely con-

verted into the work produced from system A, we have

$$Q = W \qquad\qquad (8)$$

Thus, equation (7) becomes

$$E_2 = E_1 \qquad\qquad (9)$$

From the state principle, this equation implies system A remains at stable state 1, while the heat source is transformed from the initial stable state, SS_1, to an allowed state, AS_2. In other words, it can be said that system A is a cyclic perpetual motion machine of the second kind (in contrast, a perpetual motion machine of the first kind is a device which continuously produces work without drawing upon any supply of matter or heat). The net work produced by system A in a complete cycle can be used to raise a weight; since the state of system A remains unchanged at the end of the complete cycle, the sole effect external to the heat source is the raising of a weight. Then, the weight raised could be allowed to descend to its original level, while doing work on the heat source. This results in a non-equilibrium state of the heat source at the instant when the weight is restored to its original level. Consequently, the heat source initialy in the stable state, SS_1, is transformed into some other allowed state, AS_3, without leaving any net effect on the environment. This result violates the definition of a stable state. Therefore, it is impossible to construct a cyclic perpetual motion machine of the second kind. This is one of the common statements of the second law of thermodynamics.

The law of stable equilibrium has been introduced as a single axiom of thermodynamics, from which the first law of thermodynamics, the state principle and the second law of thermodynamics can be deduced; in other words, all the general relations of classical thermodynamics can be deduced from the

single axiom. The logical structure of classical thermodynamics which may

be named the thermodynamic family tree is shown in Fig. 1; it has the law of

stable equilibrium at the head of the tree (see, e.g., Haywood, 1980).

NOMENCLATURE

E	=	energy
Q	=	heat
W	=	work
W_a	=	work involved in an adiabatic process

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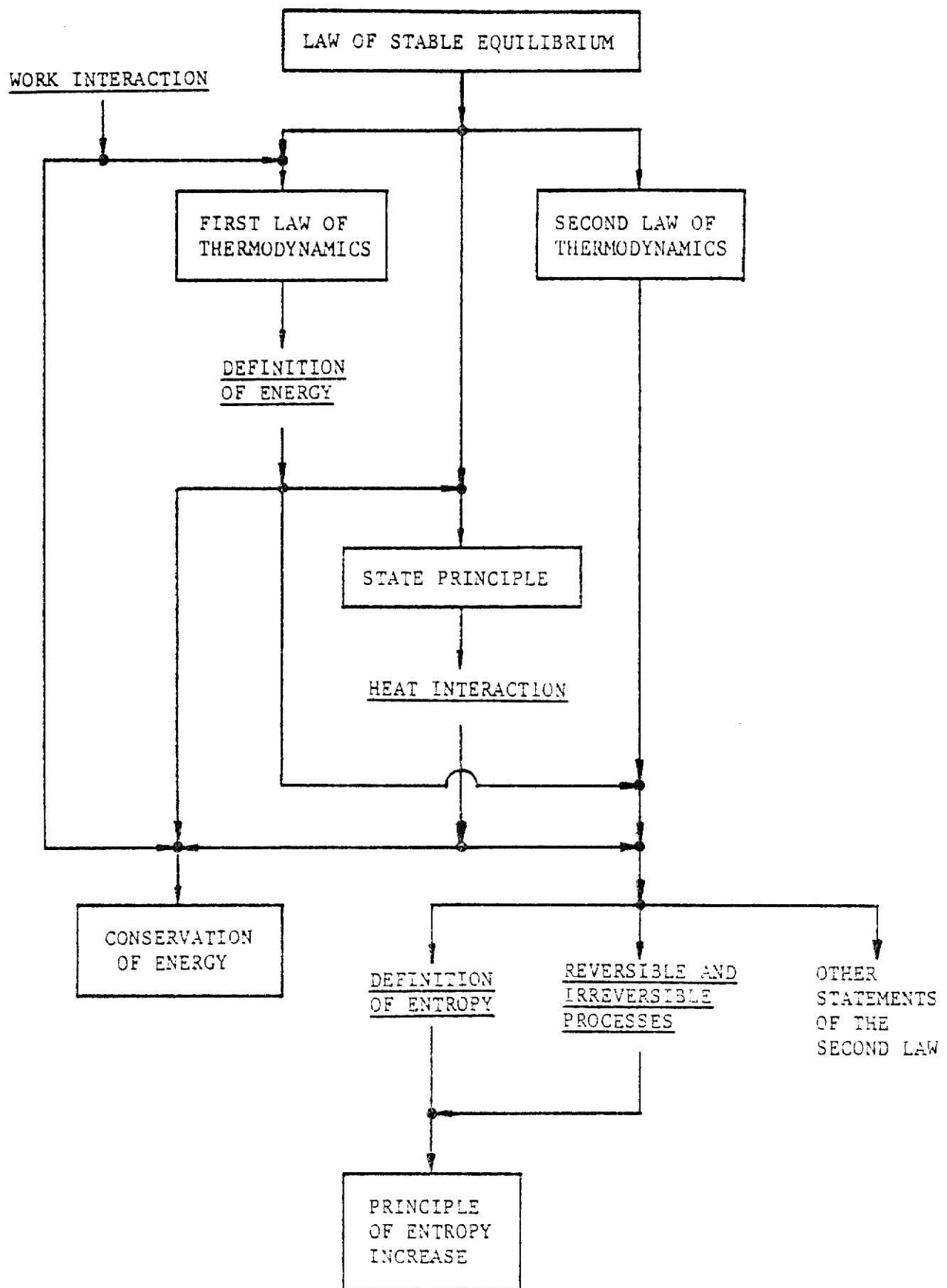
Fig. 1. Family tree of thermodynamics.

CHAPTER   3

THERMODYNAMIC MODEL

IN SYSTEM ANALYSIS

THERMODYNAMIC MODEL
IN SYSTEM ANALYSIS

In analyzing a process system from energetic points of view, it is highly desirable that we resort to the use of both the first and second laws of thermodynamics; this leads to energy and entropy balances for the system, respectively. To complete such balances, however, a reference state for measuring the thermodynamic properties need be consistently and meaningfully specified, because adoption of different reference states gives rise to different values of the properties. Once the reference state is specified. the energy and entropy contents of the system relative to the reference state can be evaluated.

Combination of the energy and entropy balances with energy and entropy contents, respectively, measured relative to the reference state gives rise naturally to the available energy balance for the system; this eventually yields the concepts and definitions of exergy and essergy. The meaningful thermodynamic efficiencies of any system can be evaluated from the mass, energy and available energy balances around the system.

REFERENCE STATE

Transformation of a system from an initial state to a final state, which is in equilibrium with the environment, is of particular interest in carrying out the thermodynamic first-law and second-law analyses. The state which is thermally, mechanically and chemically in equilibrium with the environment is named the dead state; thus, it is defined by specifying the temperature, pressure and chemical compositions of material species of the environment (see, e.g., Szargut and Petela, 1965; Riekert, 1974; Gaggioli and Petit, 1977; Fan and Shieh, 1980).

Another state conventionally chosen as a reference state is the standard state, where the temperature is the datum level temperature, the pressure is the datum level pressure and every material species is pure (see, e.g., Szargut and Petela, 1965; Riekert, 1974; Gaggioli and Petit, 1977). The environmental temperature and pressure are usually adopted as the datum level temperature and pressure; for convenience, they are often specified as 298.15 K and 1 atm, respectively.

While it is not explicitly defined in chapter 2, the environment of any system of our concern is that collection of bodies including everything external to the system. Unlike the definition employed in chapter 2, the environment defined in this chapter, which is in equilibrium with the dead state of the system of our concern, excludes the sources and sinks for material, work and heat.

MASS, ENERGY, ENTROPY AND AVAILABLE ENERGY BALANCES

The procedure for analyzing a process system is based on the law of mass conservation, and on the first and second laws of thermodynamics leading to the energy and entropy balances, respectively; combination of the last two balances gives rise to the available energy balance (see, e.g., Keenan, 1941, 1951; Rant, 1956; Denbigh, 1956, 1971; Szargut and Petela, 1965; Evans, 1969, 1980; Riekert, 1974; Gaggioli and Petit, 1977; Haywood, 1974, 1980; Fan and Shieh, 1980). For convenience, the entire system shown in Fig. 1 is considered; it contains system A (an open flow system), system M1 (a heat source), system M2 (a heat sink), system N1 (a work source), system N2 (a work sink) and the surroundings, D. System A has multiples of the input and output streams in general, and upon elimination of these streams, it is naturally transformed into a closed system. Therefore, the equations of balances for an open flow system reduce to those for the closed system.

Unsteady-State Open Flow System

System A shown in Fig. 1 is considered an unsteady-state open flow system, transforming from state 1 at t = 0 to state 2 at t = t. The detailed derivations of the mass, energy, entropy and available energy balances for this system are elaborated in appendix A. Furthermore, the macroscopic balances for an unsteady-state open flow system in general are derived from the corresponding microscopic balances in appendix E.

Mass balance

Application of the law of mass conservation to system A yields

$$\{M_{A2}(t) - M_{A1}\}$$

$$= \sum_i \left\{ \int_0^t \sum_k [(Mw)_k n_k(t)] \, dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(Mw)_k n_k(t)] \, dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(Mw)_k n_k(t)] \, dt \right\}_\ell \tag{1}$$

where

M_A = mass in system A

Mw = molecular weight

n = molar flow rate through the system including both the convective and diffusional flows at the inlet or exit of system A

k = subscript designating material species

i = subscript designating the inlet

e = subscript designating the exit

ℓ = subscript designating leakage

Energy balance

Applying the first law of thermodynamics to system A, the energy balance can be expressed as

$$[E_{A2}(t) - E_{A1}] - [(E_0)_{A2}(t) - (E_0)_{A1}]$$
$$+ P_0[V_{A2}(t) - V_{A1}] - P_0[(V_0)_{A2}(t) - (V_0)_{A1}]$$

$$= \sum_i \left\{ \int_0^t \sum_k [(\overline{\beta}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] \, dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(\overline{\beta}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] \, dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(\overline{\beta}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] \, dt \right\}_\ell$$

$$+ \int_0^t [|Q_1(t)| - |Q_2(t)| - |Q_0(t)|]dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)| - |(W_x)_0(t)|]dt \tag{2}$$

where

$\qquad E_A$ = total internal energy of system A

$\qquad V_A$ = volume of system A

$\qquad P_0$ = pressure of the environment

$\qquad |Q_1|$ = heat transmitted from system M1 to system A

$\qquad |Q_2|$ = heat transmitted from system A to system M2

$\qquad |Q_0|$ = heat loss from system A to the surroundings

$\qquad |W_1|$ = work supplied from system N1 to system A

$\qquad |W_2|$ = work supplied from system A to system N2

$\qquad |(W_x)_0|$ = work loss to the surroundings excluding that due to the expansion of the boundaries of system A

$\qquad \bar{\beta}$ = partial molar enthalpy relative to the dead state

$\bar{\beta}$ is defined as (see, e.g., Szargut and Petela, 1965; Rodriguez, 1980; Fan and Shieh, 1980)

$$\bar{\beta} \equiv \bar{h} - \bar{h}_0, \tag{3}$$

and thus, it can be written as

$$\bar{\beta} = \bar{h} - \bar{h}^0 + \bar{h}^0 - \bar{h}_0$$

$$= (\bar{h}^0 - \bar{h}_0) + [\int_{T^0}^T \left(\frac{\partial \bar{h}}{\partial T}\right)_P dT + \int_{P^0}^P \left(\frac{\partial \bar{h}}{\partial P}\right)_T dP]$$

$$= \bar{\beta}^0 + [\int_{T^0}^T \left(\frac{\partial \bar{h}}{\partial T}\right)_P dT + \int_{P^0}^P \left(\frac{\partial \bar{h}}{\partial P}\right)_T dP] \tag{4}$$

where

$$\bar{\beta}^0 \equiv \bar{h}^0 - \bar{h}_0 \tag{5}$$

From the definition of $\bar{h}$ and the Maxwell relationship, equation (4) can be rewritten as

$$\bar{\beta} = \bar{\beta}^0 + \int_{T^0}^{T} \bar{c}_p dT + \int_{P^0}^{P} [\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P] \, dP \qquad (6)$$

where superscript 0 refers to the standard state and subscript 0 to the dead state; $\bar{\beta}^0$ may be named the partial molar chemical enthalpy. The derivations of this equation and the working formula for evaluating $\bar{\beta}^0$ are elaborated in appendix B.

Entropy balance

The statement of the second law of thermodynamics for the entire system, including not only system A but also all other subsystems and the surroundings shown in Fig. 1, can be expressed as

$$\int_{0}^{t} \sigma(t)dt = [S_{A2}(t) - S_{A1}] - [(S_0)_{A2}(t) - (S_0)_{A1}]$$

$$- \left\{ \sum_i \int_{0}^{t} \sum_k [\bar{\gamma}_k(t) \, n_k(t)]dt \right\}_i$$

$$+ \sum_e \left\{ \int_{0}^{t} \sum_k [\bar{\gamma}_k(t) \, n_k(t)]dt \right\}_e$$

$$+ \sum_\ell \left\{ \int_{0}^{t} \sum_k [\bar{\gamma}_k(t) \, n_k(t)]dt \right\}_\ell$$

$$+ \int_{0}^{t} \left| -\frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0} \right| dt \qquad (7)$$

where σ is the created entropy or entropy generation in the system and $\bar{\gamma}$ is the partial molar entropy relative to the dead state; it is defined as (see, e.g., Szargut and Petela, 1965; Fan and Shieh, 1980)

$$\bar{\gamma} \equiv \bar{s} - \bar{s}_0,$$

and thus, it can be written as

$$\bar{\gamma} = \bar{s} - \bar{s}^0 + \bar{s}^0 - \bar{s}_0$$

$$= (\bar{s}^0 - \bar{s}_0) + [\int_{T^0}^{T} (\frac{\partial \bar{s}}{\partial T})_P \, dt + \int_{P^0}^{P} (\frac{\partial \bar{s}}{\partial P})_T \, dP] \tag{8}$$

By letting

$$\bar{\gamma}^0 \equiv \bar{s}^0 - \bar{s}_0 \tag{9}$$

and applying the definition of $\bar{s}$ and the Maxwell relationship to equation (8), we have

$$\bar{\gamma} = \bar{\gamma}^0 + \int_{T^0}^{T} \frac{\bar{c}_P}{T} \, dt - \int_{P^0}^{P} (\frac{\partial \bar{v}}{\partial T})_P \, dP \tag{10}$$

where $\bar{\gamma}^0$ may be called partial molar chemical entropy. The detailed derivation of this equation is shown in appendix B, including the derivation of the working formula for determining $\bar{\gamma}^0$.

Available energy balance

Combination of equation (2), the energy balance, and equation (7), the entropy balance, gives rise to

$$\{[E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)]$$

$$- [(E_0)_{A2}(t) + P_0(V_0)_{A2}(t) - T_0(S_0)_{A2}(t)]\}$$

$$- \{[E_{A1} + P_0 V_{A1} - T_0 S_{A1}] - [(E_0)_{A1} + P_0(V_0)_{A1} - T_0(S_0)_{A1}]\}$$

$$= \sum_i \left\{ \int_0^t \sum_k [(\bar{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(\bar{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(\bar{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_\ell$$

$$+ \int_0^t [|Q_1(t)|(1 - \frac{T_0}{T_{m1}}) - |Q_2(t)|(1 - \frac{T_0}{T_{m2}}) + |W_1(t)| - |W_2(t)|] dt$$

$$- \int_0^t [|(W_x)_0(t)| + (T_0 \sigma(t))] dt \tag{11}$$

The left hand-side of this expression is the change in essergy of system A, which is discussed in appendix A (also see, e.g., Evans, 1969, 1980); $\bar{\varepsilon}$ in the right-hand side is the partial molar exergy and is defined as (see, e.g., Gaggioli, 1961; Szargut and Petela, 1965; Riekert, 1974; Fan and Shieh, 1980)

$$\bar{\varepsilon} \equiv (\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0), \tag{12}$$

and thus, this equation can be transformed as

$$\bar{\varepsilon} = \bar{\varepsilon}^0 + \int_{T^0}^{T} \bar{c}_p \left(1 - \frac{T_0}{T}\right) dt$$

$$+ \int_{P^0}^{P} [\bar{v} - (T - T_0) \left(\frac{\partial \bar{v}}{\partial T}\right)_P] \, dP \tag{13}$$

where $\bar{\varepsilon}^0$ may be named partial molar chemical exergy defined as

$$\bar{\varepsilon}^0 \equiv (\bar{h}^0 - \bar{h}_0) - T_0(\bar{s}^0 - \bar{s}_0) \tag{14}$$

The derivations of equation (13) and the working formula for evaluating $\bar{\varepsilon}^0$ are detailed in appendix B.

Furthermore, the exergy may be also expressed in various ways: in terms of the Gibbs free energy, the chemical potential and the availability function ; it is derived in appendix C with a discussion of the relationship between exergy and essergy.

Steady-State Open Flow System

A system is called a steady-state open flow system if the state and velocity of the fluid entering and leaving the system are invariable with time and there is no change in the state within the system (see, e.g., Keenan, 1941; Haywood, 1980). Suppose that system A shown in Fig. 1 is a steady-state open flow system, and thus, the mass, energy, entropy and available energy balances are derived from the corresponding

balances for the unsteady-state open flow system shown in the preceding subsection; all terms representing the changes in the state properties of system A vanish, and the integrants in the balances for the unsteady-state open flow system become constant for the steady-state system.

Mass balance

From equation (1), the mass balance for the steady-state open flow system becomes

$$\sum_i [\sum_k (Mw)_k n_k]_i = \sum_e [\sum_k (Mw)_k n_k]_e + \sum_\ell [\sum_k (Mw)_k n_k]_\ell \tag{15}$$

Energy balance

From equation (2), the energy balance becomes

$$\left\{ \sum_i [\sum_k (\bar\beta + gx + \frac{u^2}{2} + \ldots)_k n_k]_i + |Q_1| + |W_1| \right\}$$

$$= \left\{ \sum_e [\sum_k (\bar\beta + gx + \frac{u^2}{2} + \ldots)_k n_k]_e + |Q_2| + |W_2| \right\}$$

$$+ \left\{ \sum_\ell [\sum_k (\bar\beta + gx + \frac{u^2}{2} + \ldots)_k n_k]_\ell \right\}$$

$$+ \left\{ |Q_0| + |(W_x)_0| \right\} \tag{16}$$

If the potential energy, kinetic energy, etc. are negligible, equation (16) reduces to

$$[\sum_i (\sum_k \bar\beta_k n_k)_i + |Q_1| + |W_1|]$$

$$= [\sum_e (\sum_k \bar\beta_k n_k)_e + |Q_2| + |W_2|] + [\sum_\ell (\sum_k \bar\beta_k n_k)_\ell]$$

$$+ [|Q_0| + |(W_x)_0|] \tag{17}$$

Suppose that i_1 (or i_2) number of the inlet streams can be identified as the streams which lose (or gain) enthalpy contents to become e_1 (or e_2) number of the exit streams and ℓ_1 (or ℓ_2) number of the leakage streams, during their passage through system A. Then,

equation (17) can be expressed as

$$\left\{ [\sum_{i_1} (\sum_k \bar{\beta}_k n_k)_{i_1} + \sum_{i_2} (\sum_k \bar{\beta}_k n_k)_{i_2}] + |Q_1| + |W_1| \right\}$$

$$= \left\{ [\sum_{e_1} (\sum_k \bar{\beta}_k n_k)_{e_1} + \sum_{e_2} (\sum_k \bar{\beta}_k n_k)_{e_2}] + |Q_2| + |W_2| \right\}$$

$$+ \left\{ [\sum_{\ell_1} (\sum_k \bar{\beta}_k n_k)_{\ell_1} + \sum_{\ell_2} (\sum_k \bar{\beta}_k n_k)_{\ell_2} \right\} + \left\{ |Q_0| + |(W_x)_0| \right\}_{(18)}$$

Since the separately identifiable material streams act either as energy sinks or as energy sources to system A, it is often convenient to rewrite this equation in the so-called incremental form, by grouping the corresponding terms, as

$$\left\{ [\sum_{i_1} (\sum_k \bar{\beta}_k n_k)_{i_1} - \sum_{e_1} (\sum_k \bar{\beta}_k n_k)_{e_1} - \sum_{\ell_1} (\sum_k \bar{\beta}_k n_k)_{\ell_1}] + [|Q_1| + |W_1|] \right\}$$

$$= \left\{ [\sum_{e_2} (\sum_k \bar{\beta}_k n_k)_{e_2} + \sum_{\ell_2} (\sum_k \bar{\beta}_k n_k)_{\ell_2} - \sum_{i_2} (\sum_k \bar{\beta}_k n_k)_{i_2}] + [|Q_2| + |W_2|] \right\}$$

$$+ \left\{ |Q_0| + |(W_x)_0| \right\} \qquad (19)$$

Entropy balance

Equation (7) reduces to

$$\sum_i (\sum_k \bar{\gamma}_k n_k)_i + \frac{|Q_1|}{T_{m1}}$$

$$= \sum_e (\sum_k \bar{\gamma}_k n_k)_e + \sum_\ell (\sum_k \bar{\gamma}_k n_k)_\ell + \frac{|Q_2|}{T_{m2}} + \frac{|Q_0|}{T_0} - \sigma \qquad (20)$$

Available energy balance

From equation (11), the available energy balance for the steady-state open flow system becomes

$$\left\{ \sum_i [\sum_k (\bar{\epsilon} + gx + \frac{u^2}{2} + \ldots)_k n_k]_i \right.$$

$$\left. + |Q_1| (1 - \frac{T_0}{T_{m1}}) + |W_1| \right\}$$

$$= \left\{ \sum_e [\sum_k (\bar{\varepsilon} + gx + \frac{u^2}{2} + \dots)_k n_k]_e \right.$$

$$+ |Q_2| (1 - \frac{T_0}{T_{m2}}) + |W_2| \bigg\}$$

$$+ \left\{ \sum_\ell [\sum_k (\bar{\varepsilon} + gx + \frac{u^2}{2} + \dots)_k n_k]_\ell \right\}$$

$$+ \left\{ |(W_x)_0| + (T_0 \sigma) \right\} \tag{21}$$

This equation can also be obtained by combination of the energy balance, equation (16), and the entropy balance, equation (20). If the potential energy, kinetic energy, etc. are negligible, equation (21) reduces to

$$[\sum_i (\sum_k \bar{\varepsilon}_k n_k)_i + |Q_1| (1 - \frac{T_0}{T_{m1}}) + |W_1|]$$

$$= [\sum_e (\sum_k \bar{\varepsilon}_k n_k)_e + |Q_2| (1 - \frac{T_0}{T_{m2}}) + |W_2|] + [\sum_\ell (\sum_k \bar{\varepsilon}_k n_k)_\ell]$$

$$+ [|(W_x)_0| + (T_0 \sigma)] \tag{22}$$

Similar to the incremental form of the energy balance, equation (19), it is often convenient to rewrite equation (22) as

$$\left\{ [\sum_{i_1} (\sum_k \bar{\varepsilon}_k n_k)_{i_1} - \sum_{e_1} (\sum_k \bar{\varepsilon}_k n_k)_{e_1} - \sum_{\ell_1} (\sum_k \bar{\varepsilon}_k n_k)_{\ell_1}] \right.$$

$$+ [|Q_1| (1 - \frac{T_0}{T_{m1}}) + |W_1|] \bigg]$$

$$= \left\{ [\sum_{e_2} (\sum_k \bar{\varepsilon}_k n_k)_{e_2} + \sum_{\ell_2} (\sum_k \bar{\varepsilon}_k n_k)_{\ell_2} - \sum_{i_2} (\sum_k \bar{\varepsilon}_k n_k)_{i_2}] \right.$$

$$+ [|Q_2| (1 - \frac{T_0}{T_{m2}}) + |W_2|] + \left\{ |(W_x)_0| + (T_0 \sigma) \right\} \tag{23}$$

Furthermore, if the leakage is negligible, equation (22) can be transformed into (see, Appendix D)

$$|W_{n,r}| = [\sum_{i} (\sum_{k} \bar{b}_k n_k)_i - \sum_{e} (\sum_{k} \bar{b}_k n_k)_e]$$

$$+ |Q_1| (1 - \frac{T_0}{T_{m1}}) - |Q_2| (1 - \frac{T_0}{T_{m2}}) \quad (24)$$

where $|W_{n,r}|$ denotes the net reversible work and b_k the partial molar availability function of substance k; they are expressed, respectively, as

$$|W_{n,r}| = |W_2| - |W_1| + |(W_x)_0| + (T_0\sigma) \quad (25)$$

and

$$\bar{b}_k = \bar{h}_k - T_0\bar{s}_k \quad (26)$$

Equation (24) is identical to the expression obtained by the so-called lost work analysis, which is discussed in appendix D (also see, e.g., Nevers and Seader, 1980; Nevers, 1982).

Unsteady-State Closed System

A closed system does not exchange materials with the surroundings; it may exchange heat and work with the surroundings. Suppose that system A shown in Fig. 1 is an unsteady-state closed system which does not contain the input and the output streams. Then, the mass, energy, entropy and available energy balances can be obtained from the corresponding balances given in the preceding subsection for the unsteady-state open flow system, by omitting all terms representing mass, energy, entropy and available energy associated with the material flows.

Mass balance

From equation (1), we have

$$M_{A2} = M_{A1} \quad (27)$$

The mass contained in the closed system, obviously, remains constant.

Energy balance

Eliminating the terms associated with the material flows in equation (2), we have

$$[E_{A2}(t) - E_{A1}] - [(E_0)_{A2}(t) - (E_0)_{A1}]$$
$$+ P_0[V_{A2}(t) - V_{A1}] - P_0[(V_0)_{A2}(t) - (V_0)_{A1}]$$

$$= \int_0^t [|Q_1(t)| - |Q_2(t)| - |Q_0(t)|]dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)| - |(W_x)_0(t)|]dt \tag{28}$$

This is the energy balance for the unsteady-state closed system, system A, with its energy contents measured relative to the dead state.

Furthermore, note that the changes in the properties of a closed system at the dead state are zero, and thus, we have

$$[(E_0)_{A2}(t) - (E_0)_{A1}] = 0$$

and

$$[(V_0)_{A2}(t) - (V_0)_{A1}] = 0$$

Substituting these expressions into equation (28), we have

$$[E_{A2}(t) - E_{A1}] + P_0[V_{A2}(t) - V_{A1}]$$

$$= \int_0^t [|Q_1(t)| - |Q_2(t)| - |Q_0(t)|]dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)| - |(W_x)_0(t)|]dt \tag{29}$$

Entropy balance

Omitting the terms associated with the material flows in equation (7), we have

$$\int_0^t \sigma(t) \, dt$$

$$= [S_{A2}(t) - S_{A1}] - [(S_0)_{A2}(t) - (S_0)_{A1}]$$

$$+ \int_0^t [- \frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0}] dt \qquad (30)$$

This is the entropy balance for the unsteady-state closed system, system A, with entropy contents measured relative to the dead state.

Again note that the changes in the properties of a closed system at the dead state are zero, and thus, we have

$$[(S_0)_{A2}(t) - (S_0)_{A1}] = 0$$

Therefore, equation (30) reduces to

$$\int_0^t \sigma(t) \, dt$$

$$= [S_{A2}(t) - S_{A1}]$$

$$+ \int_0^t [- \frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0}] \, dt \qquad (31)$$

<u>Available energy balance</u>

Eliminating the terms associated with the material flows in equation (11), we have

$$\Big\{ [E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)]$$

$$- [(E_0)_{A2}(t) + P_0 (V_0)_{A2}(t) - T_0 (S_0)_{A2}(t)] \Big\}$$

$$- \Big\{ [(E_{A1} + P_0 V_{A1} - T_0 S_{A1}] - [(E_0)_{A1} + P_0 (V_0)_{A1} - T_0 (S_0)_{A1}] \Big\}$$

$$= \int_0^t [|Q_1(t)| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2(t)| \, (1 - \frac{T_0}{T_{m2}})] dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)|] dt$$

$$- \int_0^t [|(W_x)_0(t)| + (T_0 \, \sigma(t))] dt \qquad (32)$$

This is the available energy balance for the unsteady-state closed system, system A. The left-hand side of this equation is the change in essergy of system A, which is discussed in appendix C.

Since

$$[(E_0)_{A2}(t) - (E_0)_{A1}] = 0$$
$$[(V_0)_{A2}(t) - (V_0)_{A1}] = 0$$

and

$$[(S_0)_{A2}(t) - (S_0)_{A1}] = 0,$$

equation (32) reduces to

$$[E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)]$$
$$- [E_{A1} + P_0 V_{A1} - T_0 S_{A1}]$$
$$= \int_0^t [|Q_1(t)| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2(t)| \, (1 - \frac{T_0}{T_{m2}})] dt$$
$$+ \int_0^t [|W_1(t)| - |W_2(t)|] dt$$
$$- \int_0^t [|(W_x)_0(t)| + (T_0 \, \sigma(t)] dt \qquad (33)$$

Note that the left-hand side of this equation indicates the change in the available energy contents of system A; however, an individual term grouped by square brackets by itself is not the available energy.

Steady-State Closed System

System A shown in Fig. 1 is considered a steady-state closed system. For example, suppose that heat conduction is occuring at a constant rate through a rod whose ends are fixed at different temperatures; then, the rod itself is a steady-state closed system. The mass, energy, entropy and available energy balances can be derived from the

corresponding balances for an unsteady-state closed system; the condition of steady state requires that the changes in the properties of system A depicted in Fig. 1 vanish, and the integrants in the balances for the unsteady-state open flow system become constant for the steady-state system.

Mass balance

The mass balance is same as that for an unsteady-state closed system. Thus, we have

$$M_{A2} = M_{A1} \tag{27a}$$

Energy balance

For the steady-state system, system A, equation (28) reduces to

$$[|Q_1| + |W_1|] = [|Q_2| + |W_2|] + [|Q_0| + |(W_x)_0|] \tag{34}$$

Entropy balance

From equation (30), the entropy balance is expressed as

$$\frac{|Q_1|}{T_{m1}} = \frac{|Q_2|}{T_{m2}} + \frac{|Q_0|}{T_0} - \sigma \tag{35}$$

Available energy balance

From equation (32), we have

$$[|Q_1| \ (1 - \frac{T_0}{T_{m1}}) + |W_1|]$$

$$= [|Q_2| \ (1 - \frac{T_0}{T_{m2}}) + |W_2|] + [(T_0\sigma) + |(W_x)_0|] \tag{36}$$

THERMODYNAMIC EFFICIENCY

Qualitatively speaking, the efficiency of a system is the effectively utilized fraction of mass, energy, available energy or any other quantity or commodity, which has been supplied to the system. From the thermodynamic point of view, three broad classes of efficiencies can be defined: they are the mass utilization efficiency and the first-law and second-law efficiencies. As the most practical case, these efficiencies are defined for the steady-state open flow system, system A, shown in Fig. 1.

Mass Utilization Efficiency

The mass balance for system A is expressed by equation (15):

$$\sum_i [\sum_k (Mw)_k n_k]_i = \sum_e [\sum_k (Mw)_k n_k]_e + \sum_\ell [\sum_k (Mw)_k n_k]_\ell \tag{37}$$

It is not uncommon that one or more of the exit streams are discarded because they contain by-products considered to be useless or wastes. Therefore, equation (37) can be conveniently rewritten as

$$\Sigma M_i = \Sigma M_{e,u} + \Sigma M_{e,d} + \Sigma M_\ell \tag{38}$$

In this expression, the left-hand side, ΣM_i, is the overall input of mass, corresponding to the left-hand side of equation (37); the first and second terms in the right-hand side, $\Sigma M_{e,u}$ and $\Sigma M_{e,d}$, are the usable and discarded parts of the mass output, respectively, collectively corresponding to the first term in the right-hand side of equation (37); and the third term, ΣM_ℓ, is the leakage, corresponding to the second term in the right-hand side of equation (37).

From equation (38), the mass utilization efficiency can be expressed as

$$\eta_m = \frac{\Sigma \, M_{e,u}}{\Sigma M_i} \qquad (39)$$

First-Law Efficiency

By assuming that potential energy, kinetic energy, etc. are negligible, the energy balance is expressed by equation (17):

$$[\sum_i (\sum_k \bar{\beta}_k \, n_k)_i + |Q_1| + |W_1|]$$

$$= [\sum_e (\sum_k \bar{\beta}_k \, n_k)_e + |Q_2| + |W_2|] + [\sum_\ell (\sum_k \bar{\beta}_k \, n_k)_\ell]$$

$$+ [|Q_0| + |(W_x)_0|] \qquad (40)$$

When one or more of the exit streams are discarded to the environment as wastes, equation (40) can be conveniently expressed as

$$[\Sigma(H_{av})_i] = [\Sigma(H_{av})_{e,u} + \Sigma(H_{av})_{e,d}] + [\Sigma(H_{av})_\ell] + [\Sigma(H_{av})_c]$$

$$(41)$$

The left-hand side, $\Sigma(H_{av})_i$, in this equation is the total energy input in forms of enthalpy, heat and work; the first term in the right-hand side, $\Sigma(H_{av})_{e,u}$, the usable portion of the energy output in forms of enthalpy, heat and work; the second term, $\Sigma(H_{av})_{e,d}$, the portion of the energy output associated with the discarded material streams; the third term, $\Sigma(H_{av})_\ell$, the energy associated with the material leakage; and the last term, $\Sigma(H_{av})_c$, the energy consumption which consists of heat loss through the wall, $|Q_0|$, and the work loss, $|(W_x)_0|$. There exists a one-to-one correspondence between the equivalent terms in equations (40) and (41), all bracketed by [ ].

The so-called incremental form of the energy balance can be expressed by equation (19):

$$\left\{ \left[\sum_{i_1} (\sum_k \bar{\beta}_k n_k)_i - \sum_{e_1} (\sum_k \bar{\beta}_k n_k)_{e_1} - \sum_{\ell_1} (\sum_k \bar{\beta}_k n_k)_{\ell_1} \right] + [|Q_1| + |W_1|] \right\}$$

$$= \left\{ \left[\sum_{e_2} (\sum_k \bar{\beta}_k n_k)_{e_2} + \sum_{\ell_2} (\sum_k \bar{\beta}_k n_k)_{\ell_2} - \sum_{i_2} (\sum_k \bar{\beta}_k n_k)_{i_2} \right] + [|Q_2| + |W_2|] \right\}$$

$$+ \left\{ |Q_0| + |(W_x)_0| \right\} \tag{42}$$

This equation can be rewritten as

$$\left\{ \Sigma (H_{av})_i \right\}_D = \left\{ \Sigma (H_{av})_e \right\}_D + \left\{ \Sigma (H_{av})_c \right\} \tag{43}$$

where $\{\Sigma (H_{av})_i\}_D$ is the energy transferred to system A from energy sources, including heat sources, work sources and process streams which lose energy contents during their passage through the system, $\{\Sigma (H_{av})_e\}_D$ is the energy transferred by system A to energy sinks, including heat sinks, work sinks and process streams which gain energy contents during their passage through the system, and $\{\Sigma (H_{av})_c\}$ is the energy consumption due to the loss through the walls of system A. In other words, there exists a one-to-one correspondence between the equivalent terms in equations (42) and (43), all grouped by brackets, { }.

The first-law process and incremental (or extractive) efficiencies of a process system can be expressed from equations (41) and (43), respectively, as

$$(\eta_1)_P = \frac{[\Sigma (H_{av})_{e,u}]}{[\Sigma (H_{av})_i]} \tag{44}$$

and

$$(\eta_1)_D = \frac{\{\Sigma (H_{av})_e\}_D}{\{\Sigma (H_{av})_i\}_D} \tag{45}$$

Second-Law Efficiency

The available energy balance around system A, with negligible potential energy, kinetic energy, etc. is expressed by equation (22):

$$[\sum_i (\sum_k \bar{\epsilon}_k n_k)_i + |Q_1| (1 - \frac{T_0}{T_{m1}}) + |W_1|]$$

$$= [\sum_e (\sum_k \bar{\epsilon}_k n_k)_e + |Q_2| (1 - \frac{T_0}{T_{m2}}) + |W_2|] + [\sum_\ell (\sum_k \bar{\epsilon}_k n_k)_\ell]$$

$$+ [|(W_x)_0| + (T_0 \sigma)] \tag{46}$$

Similar to equation (41), equation (46) can be compactly expressed as

$$[\Sigma(A_{ex})_i] = [\Sigma(A_{ex})_{e,u} + \Sigma(A_{ex})_{e,d}] + [\Sigma(A_{ex})_\ell] + [\Sigma(A_{ex})_{dis}] \tag{47}$$

where subscript dis stands for the available energy dissipation due to all kinds of irreversibility. Obviously, $[\Sigma(A_{ex})_i]$ corresponds to the left-hand side of equation (15), and $[\Sigma(A_{ex})_{e,u} + \Sigma(A_{ex})_{e,d}]$, $[\Sigma(A_{ex})_\ell]$ and $[\Sigma(A_{ex})_{dis}]$ correspond, respectively, to the first, second and third terms in the right-hand side of equation (46), all bracketed by [ ]. Again similar to equations (42) and (43), equation (46) can be rewritten as

$$\left\{ [\sum_{i_1} (\sum_k \bar{\epsilon}_k n_k)_{i_1} - \sum_{e_1} (\sum_k \bar{\epsilon}_k n_k)_{e_1} - \sum_{\ell_1} (\sum_k \bar{\epsilon}_k n_k)_{\ell_1}] \right.$$

$$\left. + [|Q_1| (1 - \frac{T_0}{T_{m1}}) + |W_1|] \right\}$$

$$= \left\{ [\sum_{e_2} (\sum_k \bar{\epsilon}_k n_k)_{e_2} + \sum_{\ell_2} (\sum_k \bar{\epsilon}_k n_k)_{\ell_2} - \sum_{i_2} (\sum_k \bar{\epsilon}_k n_k)_{i_2}] \right.$$

$$\left. + [|Q_2| (1 - \frac{T_0}{T_{m2}}) + |W_2|] \right\}$$

$$+ \left\{ |(W_x)_0| + (T_0 \sigma) \right\} \tag{48}$$

and

$$\{\Sigma(A_{ex})_i\}_D = \{\Sigma(A_{ex})_e\}_D + \{\Sigma(A_{ex})_{dis}\} \tag{49}$$

where $\{\Sigma(A_{ex})_i\}_D$ is the availabe energy transferred to system A from the energy sources, including heat sources, work sources and process streams which lose available energy contents during their passage through the

system, $\{\Sigma(A_{ex})_e\}_D$ is the available energy transferred from system A to the energy sinks, including heat sinks, work sinks and process streams which gain available energy contents during their passage through the system, and $\{\Sigma(A_{ex})_{dis}\}$ is the available energy dissipation. In other words, there exists a one-to-one correspondence between the equivalent terms in equations (48) and (49), all grouped by brackets, { }.

The second-law process and incremental efficiencies can be expressed from equations (47) and (49), respectively, as

$$(\eta_2)_P = \frac{[\Sigma(A_{ex})_{e,u}]}{[\Sigma(A_{ex})_i]} \tag{50}$$

and

$$(\eta_2)_D = \frac{\{\Sigma(A_{ex})_e\}_D}{\{\Sigma(A_{ex})_i\}_D} \tag{51}$$

The expressions of the efficiencies derived for a steady-state open flow system reduce to those for a steady-state closed system in a straightforward manner. Furthermore, since accumulation (or reduction) of mass, energy or available energy in the system raises (or lowers) the potential capable to do work, it should be added to the useful output (or the input). Thus, the efficiencies for an unsteady-state open flow or closed system can be derived by the same procedure as given in this section.

The thermodynamic process efficiency as defined by equation (44) or (50) is mainly concerned with the conservation of energy or available energy, and it is useful for assessing systems which process raw materials to obtain fuel or useful products. On the other hand, the thermodynamic incremental efficiency as defined by equation (45) or (51)

is concerned mainly with the transformation of energy or available energy, and it is preferred for evaluating thermodynamic efficiencies of systems which generate work or which exchange energy or available energy.

Obviously, thermodynamic efficiencies can be defined in a variety of ways different from those given in this section; nevertheless, their significance is best understood in the light of the mass, energy and available evergy balances presented in the preceding section. Naturally, strict caustion need be exercised in comparing the thermodynmaic efficiencies based on different definitions.

NOMENCLATURE

0	=	subscript representing the dead state
0	=	superscript representing the standard state
A	=	system A
$(A_{ex})_i$	=	available energy input per unit time, J/sec
$(A_{ex})_{dis}$	=	available energy dissipation per unit time, J/sec
$(A_{ex})_{e,d}$	=	discarded portion of the available energy output per unit time, J/sec
$(A_{ex})_{e,u}$	=	usable portion of the available energy output per unit time, J/sec
$(A_{ex})_\ell$	=	available energy leakage per unit time, J/sec
$\{(A_{ex})_e\}_D$	=	available energy transferred from system A to energy sinks per unit time, J/sec
$\{(A_{ex})_i\}_D$	=	available energy transferred from energy sources to system A per unit time, J/sec
E	=	total internal energy, J
e	=	output streams
gx	=	specific potential energy, J/kmol
$(H_{av})_c$	=	energy consumption per unit time, J/sec
$(H_{av})_{e,d}$	=	discarded portion of the energy output per unit time, J/sec
$(H_{av})_{e,u}$	=	usable portion of the energy output per unit time, J/sec
$(H_{av})_i$	=	energy input per unit time, J/sec
$(H_{av})_\ell$	=	energy leakage per unit time, J/sec
$\{(H_{av})_e\}_D$	=	energy transferred from system A to energy sinks per unit time, J/sec
$\{(H_{av})_i\}_D$	=	energy transferred from energy sources to system A per unit time, J/sec

$\bar{h}$	=	partial molar enthalpy, J/kmol
i	=	input streams
k	=	material species
ℓ	=	leakage
$M_{e,d}$	=	discarded part of mass output per unit time, kg/sec
$M_{e,u}$	=	usable part of mass output per unit time, kg/sec
M_i	=	mass input per unit time, kg/sec
M_ℓ	=	mass leakage per unit time, kg/sec
Mw	=	molecular weight, kg/kmol
n	=	molar flow rate including both convective and diffusional flows, kmol/sec
P	=	pressure, atm
$\lvert Q_0 \rvert$	=	heat loss to the environment per unit time, J/sec
$\lvert Q_1 \rvert$	=	heat transmitted from system M1 to system A per unit time, J/sec
$\lvert Q_2 \rvert$	=	heat transmitted from system A to system M2 per unit time, J/sec
S	=	entropy, J/K
$\bar{s}$	=	partial molar entropy, J/kmol·K
T	=	temperature of system A, K
T_{m1}	=	temperature of system M1, K
T_{m2}	=	temperature of system M2, K
$u^2/2$	=	specific kinetic energy, J/kmol
v	=	volume, m^3
$\lvert (W_x)_0 \rvert$	=	work loss to the environment except that due to the expansion of the boundaries of system A per unit time, J/sec

$\lvert W_1 \rvert$	=	work supplied from the work source, system N1, to system A per unit time, J/sec
$\lvert W_2 \rvert$	=	work supplied from system A to the work source, system N2 per unit time, J/sec

GREEK

$\overline{\beta}^0$	=	partial molar enthalpy relative to the dead state, J/kmol
$\overline{\beta}^0$	=	partial molar chemical enthalpy, J/kmol
$\overline{\gamma}^0$	=	partial molar entropy relative to the dead state, J/kmol·K
$\overline{\gamma}^0$	=	partial molar chemical entropy, J/kmol·K
$\overline{\varepsilon}^0$	=	partial molar exergy, J/kmol
$\overline{\varepsilon}^0$	=	partial molar chemical exergy, J/kmol
η_m	=	mass utilization efficiency
$(\eta_1)_D$	=	thermodynamic first-law incremental efficiency
$(\eta_1)_P$	=	thermodynamic first-law process efficiency
$(\eta_2)_D$	=	thermodynamic second-law incremental efficiency
$(\eta_2)_P$	=	thermodynamic second-law process efficiency
σ	=	created entropy per unit time, J/K·sec

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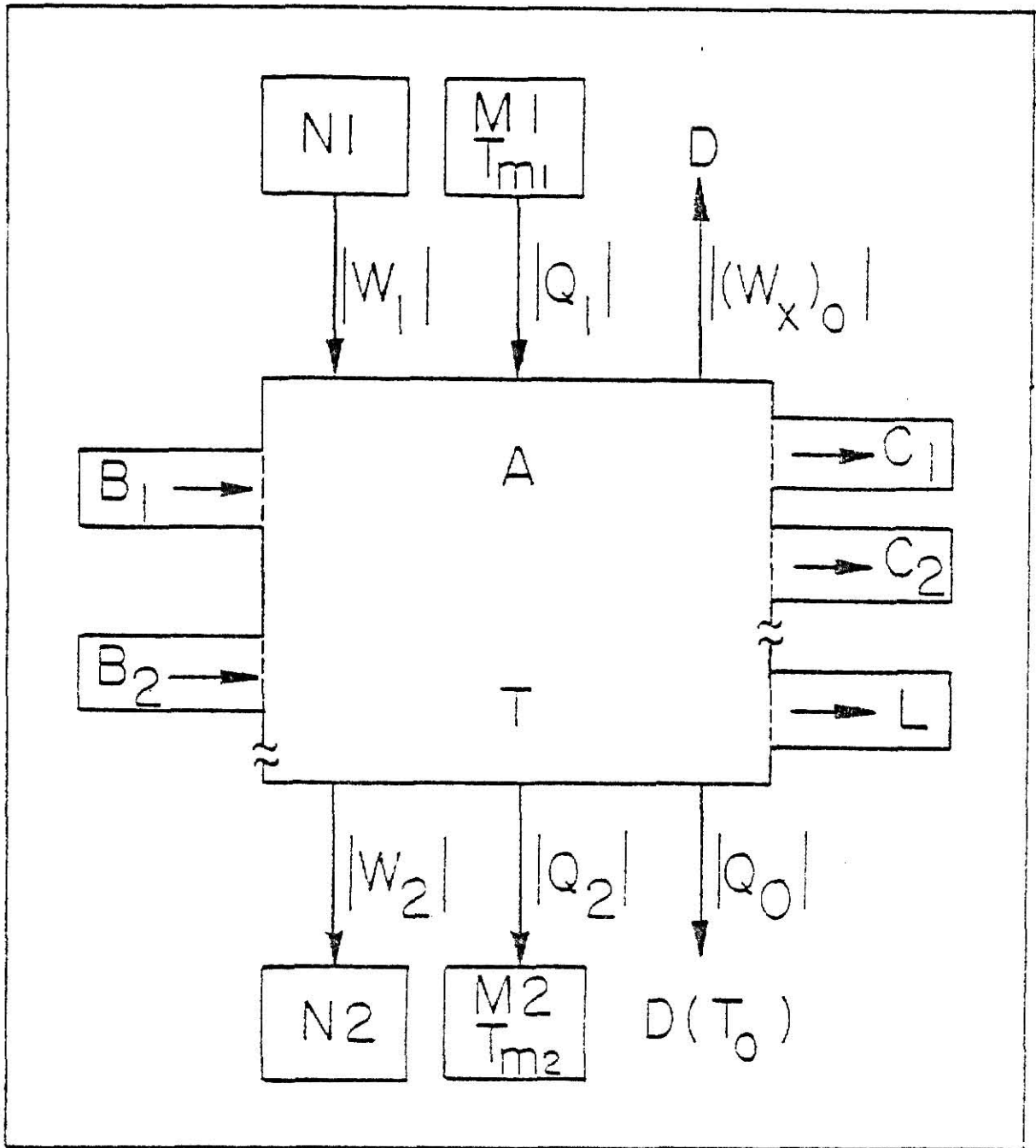
Fig. 1. Schematic diagram of an open flow system.

CHAPTER 4

THERMODYNAMIC ANALYSIS OF

A COUNTER-CURRENT HEAT EXCHANGER

THERMODYNAMIC ANALYSIS OF
A COUNTER-CURRENT HEAT EXCHANGER

A counter-current heat exchanger under consideration, which is a steady-state open flow system, is shown in Fig. 1. For simplicity, it is assumed that each stream consists of a pure material and no phase change occurs in the stream during the passage through the system.

MASS BALANCE

Application of the law of mass conservation leads to

$$[(Mw)_h \, n_h]_i \; + \; [(Mw)_c \, n_c]_i$$

$$= [(Mw)_h \, n_h]_e \; + \; [(Mw)_c \, n_c]_e + [(Mw)_h \, n_h]_\ell + [(Mw)_c \, n_c]_\ell \tag{1}$$

where

Mw = molecular weight, kg/k mol

n = molar flow rate including both the convective and diffusional flows, k mol/sec,

and subscripts stand for:

i = inlet

e = exit

h = hot stream

c = cold stream

ℓ = leakage

Note that

$$(Mw)_{h,i} = (Mw)_{h,e} = (Mw)_h \tag{2}$$

and

$$(Mw)_{c,i} = (Mw)_{c,e} = (Mw)_c \tag{3}$$

and thus, eqn. (A4-1) becomes

$$(Mw)_h \, n_{h,i} + (Mw)_c \, n_{c,i}$$

$$= (Mw)_h \, n_{h,e} + (Mw)_c \, n_{c,e} + (Mw)_h \, n_{h,\ell} + (Mw)_c \, n_{h,\ell} \tag{4}$$

Furthermore, assuming that no leakage exists, the material balance can be reduced to the expressions:

$$n_{h,i} = n_{h,e} = n_h \tag{5}$$

and

$$n_{c,i} = n_{c,e} = n_c \tag{6}$$

ENERGY BALANCE

Application of the first law of thermodynamics to the system having negligible potential energy, kinetic energy, etc., and no leakage, leads to

$$0 = [(\beta_h \, n_h)_i + (\beta_c \, n_c)_i] - [(\beta_h n_h)_e + (\beta_c n_c)_e]$$

$$+ |W_{P1}| + |W_{P2}| - |(W_x)_0| - |Q_0| \tag{7}$$

Because of equations (5) and (6), this equation becomes

$$0 = (\beta_{h,i} n_h + \beta_{c,i} n_c) - (\beta_{h,e} n_h + \beta_{c,e} n_c)$$

$$+ |W_{P1}| + |W_{P2}| - |Q_0| - |(W_x)_0| \qquad (8)$$

where

$|W_{P1}|$ = work supplied to pump P1

$|W_{P2}|$ = work supplied to pump P2

$|(W_x)_0|$ = work loss from the walls of the system to the environment except that due to the expansion of the boundaries of the system

$|Q_0|$ = heat loss from the walls of the system to the environment

β = specific enthalpy relative to the dead state

β is defined as (see, e.g., Szargut and Petela, 1965; Fan and Shieh, 1980)

$$\beta \equiv h - h_0 \qquad (9)$$

and its dependence on temperature and pressure is shown to be:

$$\beta = (h - h^0) + (h^0 - h_0)$$

$$= (h^0 - h_0) + [\int_{T^0}^{T} (\frac{\partial h}{\partial T})_P \, dT + \int_{P^0}^{P} (\frac{\partial h}{\partial P})_T \, dP]$$

$$= (h^0 - h_0) + \int_{T^0}^{T} c_P \, dT + \int_{P^0}^{P} [v - T(\frac{\partial v}{\partial T})_P] \, dP \qquad (10)$$

where superscript 0 refers to the standard state and subscript 0 to the dead state.

By letting,

$$\beta^0 = h^0 - h_0 \qquad (11)$$

$$\beta_T = \int_{T^0}^{T} c_P \, dT \qquad (12)$$

and

$$\beta_P = \int_{P0}^{P} [v - T(\frac{\partial v}{\partial T})_P] \, dP \qquad (13)$$

equation (10) is expressed as

$$\beta = \beta^0 + \beta_T + \beta_P \qquad (14)$$

ENTROPY BALANCE

Application of the second law of thermodynamics to the system leads to

$$0 = [(\gamma_h n_h)_i + (\gamma_c n_c)_i] - [(\gamma_h n_h)_e + (\gamma_c n_c)_e] - \frac{|Q_0|}{T_0} + \sigma \qquad (15)$$

Combining this expression with equations (5) and (6), we have

$$\sigma = -(\gamma_{h,i} n_h + \gamma_{c,i} n_c) + (\gamma_{h,e} n_h + \gamma_{c,e} n_c) + \frac{|Q_0|}{T_0} \qquad (16)$$

where

σ = total entropy created

γ = specific entropy relative to the dead state

γ is defined as (see, e.g., Szargut and Petela, 1965; Fan and Shieh, 1980)

$$\gamma \equiv s - s_0 \qquad (17)$$

and its dependence on the temperature and pressure can be shown to be:

$$\gamma = (s - s^0) + (s^0 - s_0)$$

$$= (s^0 - s_0) + [\int_{T^0}^{T} (\frac{\partial s}{\partial T})_P \, dT + \int_{P0}^{P} (\frac{\partial s}{\partial P})_T \, dP]$$

$$= (s^0 - s_0) + \int_{T^0}^{T} \frac{c_P}{T} \, dT - \int_{P0}^{P} (\frac{\partial v}{\partial T})_P \, dP \qquad (18)$$

Thus, by letting

$$\gamma^0 = s^0 - s_0 \tag{19}$$

$$\gamma_T = \int_{T^0}^{T} \frac{c_p}{T} \, dT \tag{20}$$

and

$$\gamma_P = - \int_{P^0}^{P} \left(\frac{\partial v}{\partial T}\right)_P \, dP, \tag{21}$$

equation (18) can be rewritten as

$$\gamma = \gamma^0 + \gamma_T + \gamma_P \tag{22}$$

AVAILABLE ENERGY BALANCE

Eliminating $|Q_0|$ from equations (8) and (16), we have

$$(T_0 \sigma) = [n_h (\beta_{h,i} - T_0 \gamma_{h,i}) + n_c (\beta_{c,i} - T_0 \gamma_{c,i})]$$
$$- [n_h (\beta_{h,e} - T_0 \gamma_{h,e}) + n_c (\beta_{c,e} - T_0 \gamma_{c,e})]$$
$$+ [|W_{P1}| + |W_{P2}| - |(W_x)_0|] \tag{23}$$

Rearrangement gives

$$[(T_0 \sigma) + |(W_x)_0|] = (n_h \varepsilon_{h,i} + n_c \varepsilon_{c,i}) - (n_h \varepsilon_{h,e} + n_c \varepsilon_{c,e})$$
$$+ |W_{P1}| + |W_{P2}| \tag{24}$$

where ε is the specific exergy; it is defined as (see, e.g., Keenan, 1941; Gaggioli, 1961; Szargut and Petela, 1965; Riekert, 1974; Fan and Shieh, 1980)

$$\varepsilon \equiv (h - h_0) - T_0(s - s_0)$$

$$= \beta - T_0 \gamma \qquad\qquad (25)$$

and, from equations (11) through (14) and equations (19) through (22), its temperature and pressure dependence is

$$\varepsilon = (\beta^0 - T_0 \gamma^0) + \int_{T^0}^{T} c_p \left(1 - \frac{T_0}{T}\right) dT$$

$$+ \int_{P^0}^{P} \left[v - (T - T_0)\left(\frac{\partial v}{\partial T}\right)_P\right] dP \qquad\qquad (26)$$

Therefore, by letting

$$\varepsilon^0 = (\beta^0 - T_0 \gamma^0) \qquad\qquad (27)$$

$$\varepsilon_T = \int_{T^0}^{T} c_p \left(1 - \frac{T_0}{T}\right) dT \qquad\qquad (28)$$

and

$$\varepsilon_P = \int_{P^0}^{P} \left[v - (T - T_0)\left(\frac{\partial v}{\partial T}\right)_P\right] dP, \qquad\qquad (29)$$

equation (26) becomes

$$\varepsilon = \varepsilon^0 + \varepsilon_T + \varepsilon_P \qquad\qquad (30)$$

IRREVERSIBILITY

Substituting equation (30) into equation (24), we have

$$[(T_0 \sigma) + |(W_x)_0|]$$

$$= \{ n_h [(\varepsilon^0)_{h,i} + (\varepsilon_T)_{h,i} + (\varepsilon_P)_{h,i}] + n_c [(\varepsilon^0)_{c,i} + (\varepsilon_T)_{c,i} + (\varepsilon_P)_{c,i}] \}$$

$$- \{ n_h [(\varepsilon^0)_{h,e} + (\varepsilon_T)_{h,e} + (\varepsilon_P)_{h,e}] + n_c [(\varepsilon^0)_{c,e} + (\varepsilon_T)_{c,e} + (\varepsilon_P)_{c,e}] \}$$

$$+ |W_{P1}| + |W_{P2}| \tag{31}$$

Note that

$$(\varepsilon^0)_{h,i} = (\varepsilon^0)_{h,e} \tag{32}$$

and

$$(\varepsilon^0)_{c,i} = (\varepsilon^0)_{c,e} \tag{33}$$

and thus, equation (31) becomes

$$[(T_0 \sigma) + (W_x)_0]$$

$$= n_h \{ [(\varepsilon_T)_{h,i} - (\varepsilon_T)_{h,e}] + [(\varepsilon_P)_{h,i} - (\varepsilon_P)_{h,e}] \}$$

$$+ n_c \{ [(\varepsilon_T)_{c,i} - (\varepsilon_T)_{c,e}] + [(\varepsilon_P)_{c,i} - (\varepsilon_P)_{c,e}] \}$$

$$+ |W_{P1}| + |W_{P2}| \tag{34}$$

Two special cases are considered:

a. Suppose that the pressure drop in each stream between the inlet and outlet is negligible; we have

$$(\varepsilon_P)_{h,i} = (\varepsilon_P)_{h,e} \tag{35}$$

and

$$(\varepsilon_p)_{c,i} = (\varepsilon_p)_{c,e} \tag{36}$$

and thus, equation (31) becomes

$$[(T_0 \sigma) + |(W_x)_0|]$$

$$= n_h [(\varepsilon_T)_{h,i} - (\varepsilon_T)_{h,e}] + n_c [(\varepsilon_T)_{c,i} - (\varepsilon_T)_{c,e}]$$

$$+ |W_{P1}| + |W_{P2}| \tag{37}$$

If the specific heat, c_P, is constant in each stream, equation (28) becomes

$$\varepsilon_T = c_P [(T - T^0) - T_0 \ln \frac{T}{T^0}] \tag{38}$$

Substituting this expression into equation (37)

$$[(T_0 \sigma) + |(W_x)_0|]$$

$$= n_h c_{P,h} [(T_{h,i} - T_{h,e}) - T_0 \ln \frac{T_{h,i}}{T_{h,e}}]$$

$$+ n_c c_{P,c} [(T_{c,i} - T_{c,e}) - T_0 \ln \frac{T_{c,i}}{T_{c,e}}]$$

$$+ |W_{P1}| + |W_{P2}| \tag{39}$$

b. Suppose that the energy loss from the walls of the system to the environment, $[|Q_0| + |(W_x)_0|]$, is negligible; the energy balance, equation (8) becomes

$$0 = (\beta_{h,i} n_h + \beta_{c,i} n_c) - (\beta_{h,e} n_h + \beta_{c,e} n_c)$$

$$+ |W_{P1}| + |W_{P2}| \tag{40}$$

Substitution of equation (14) into this expression gives

$$0 = \{n_h \left[(\beta^{\hat{0}})_{h,i} + (\beta_T)_{h,i} + (\beta_P)_{h,i}\right] + n_c\left[(\beta^0)_{c,i} + (\beta_T)_{c,i} + (\beta_P)_{c,i}\right]\}$$

$$- \{n_h\left[(\beta^0)_{h,e} + (\beta_T)_{h,e} + (\beta_P)_{h,e}\right] + n_c\left[(\beta^0)_{c,e} + (\beta_T)_{c,e}\right.$$

$$\left. + (\beta_P)_{c,e}\right]\} + |W_{P1}| + |W_{P2}| \tag{41}$$

Note that

$$(\beta^0)_{h,i} = (\beta^0)_{h,e} \tag{42}$$

and

$$(\beta^0)_{c,i} = (\beta^0)_{c,e} \tag{43}$$

and thus, equation (41) becomes

$$0 = n_h\{[(\beta_T)_{h,i} - (\beta_T)_{h,e}] + [(\beta_P)_{h,i} - (\beta_P)_{h,e}]\}$$

$$+ n_c\{[(\beta_T)_{c,i} - (\beta_T)_{c,e}] + [(\beta_P)_{c,i} - (\beta_P)_{c,e}]\}$$

$$+ |W_{P1}| + |W_{P2}| \tag{44}$$

If the specific heat of each stream is constant and the pressure drop
along each stream between the inlet and outlet is negligible, we have

$$\beta_T = c_p(T-T^0) \tag{45}$$

and

$$(\beta_P)_i = (\beta_P)_e \tag{46}$$

and thus, equation (44) becomes

$$0 = n_h c_{P,h} (T_{h,i} - T_{h,e}) + n_c c_{P,c} (T_{c,i} - T_{c,e})$$

$$+ |W_{P1}| + |W_{P2}| \tag{47}$$

Substitution of this equation into equation (39) yields

$$(T_0 \sigma) = T_0 \left[n_h c_{P,h} \ln \frac{T_{h,e}}{T_{h,i}} + n_c c_{P,c} \ln \frac{T_{c,e}}{T_{c,i}}\right] \tag{48}$$

THERMODYNAMIC EFFICIENCIES .

Qualitatively speaking, the efficiency of any process system can be expressed as the effectively utilized fraction of mass, energy or available energy which has been supplied to the system. Therefore, three broad classes of efficiencies can be defined. They are the mass utilization efficiency and the thermodynamic first-law and second-law efficiencies.

From the mass balance, equation (1), the energy balance, equation (8) and the available energy balance, equation (24), the mass utilization efficiency, η_m, and the thermodynamic first-law and second-law process efficiencies, $(\eta_1)_p$ and $(\eta_2)_p$, are expressed, respectively, as

$$\eta_m = \frac{(\text{usable mass output})}{(\text{mass input})} \tag{49}$$

$$(\eta_1)_p = \frac{(\text{usable energy output})}{(\text{energy input})} \tag{50}$$

$$(\eta_2)_p = \frac{(\text{usable available energy output})}{(\text{available energy input})} \tag{51}$$

For instance, if both the hot-stream and cold-stream outputs are recovered or usable, η_m, $(\eta_1)_p$ and $(\eta_2)_p$ are:

$$\eta_m = \frac{[(Mw)_h \, n_h]_e + [(Mw)_c \, n_c]_e}{[(Mw)_h \, n_h]_i + [(Mw)_c \, n_c]_i} \tag{52}$$

$$(\eta_1)_p = \frac{(\beta_{h,e} \, n_h + \beta_{c,e} \, n_c)}{(\beta_{h,i} \, n_h + \beta_{c,i} \, n_c) + |W_{p1}| + |W_{p2}|} \tag{53}$$

and

$$(\eta_2)_p = \frac{(\varepsilon_{h,e} \, n_h + \varepsilon_{c,e} \, n_c)}{(\varepsilon_{h,i} \, n_h + \varepsilon_{c,i} \, n_c) + |W_{p1}| + |W_{p2}|} \tag{54}$$

Also from equations (8) and (24), the thermodynamic first-law and second-law incremental efficiencies, $(\eta_1)_D$ and $(\eta_2)_D$, are derived, respectively, as

$$(\eta_1)_D = \frac{n_c \, (\beta_{c,e} - \beta_{c,i})}{n_h \, (\beta_{h,i} - \beta_{h,e}) + |W_{P1}| + |W_{P2}|} \tag{55}$$

and

$$(\eta_2)_D = \frac{n_c \, (\varepsilon_{c,e} - \varepsilon_{c,i})}{n_h \, (\varepsilon_{h,i} - \varepsilon_{h,e}) + |W_{P1}| + |W_{P2}|} \tag{56}$$

Note that all the development presented so far, which is for single-component systems, can be extended to multi-component systems in a straight-forward way.

NUMERICAL EXAMPLE

A gas-to-air heat exchanger is often used to preheat combustion air through heat exchange with hot flue gas. The flue gas has the following characteristics.

$$M_h = 20,000 \quad \text{kg/hr}$$

$$T_{h,i} = 1033.15 \text{ K}$$

$$T_{h,e} = 853.15 \text{ K}$$

$$c_{P,h} = 0.35 \quad \text{kcal/kg K}$$

$$P_{h,i} = 1.0 \quad \text{atm}$$

$$P_{h,e} = 1.079 \quad \text{atm}$$

$$\beta^0 = 147.2 \quad \text{kcal/kg}$$

$$\varepsilon^0 = 45.93 \quad \text{kcal/kg}$$

$$Mw = 25.6 \quad \text{kg/kmol}$$

The characteristics of the combustion air are as follows:

$$M_c = 9,500 \quad \text{kg/hr}$$

$$T_{c,i} = 298.15 \text{ K}$$

$$T_{c,e} = 813.15 \text{ K}$$

$$c_{P,c} = 0.23 \quad \text{kcal/kg K}$$

$$P_{c,i} = 1.0 \quad \text{atm}$$

$$P_{c,e} = 1.094 \quad \text{atm}$$

$$\beta^0 = 0$$

$$\varepsilon^0 = 0$$

$$Mw = 29 \quad \text{kg/kmol}$$

Work requirements for blowers P1 and P2, are as follows:

$$\left| W_{P1} \right| = 44,100 \quad \text{kcal/hr}$$

$$\left| W_{P2} \right| = 18,500 \quad \text{kcal/hr}$$

Assuming ideal gas behavior for both the flue gas and combustion air, we have from equations (12), (13), (28) and (29)

$$\beta_T = c_p (T - T^0)$$

$$\beta_P = \int_{p0}^{P} [v - T \frac{R}{P}] dP$$

$$= 0$$

$$\varepsilon_T = c_p [(T - T^0) - T_0 \ln \frac{T}{T^0}]$$

and

$$\varepsilon_P = \int_{p0}^{P} [v - (T - T_0) \frac{R}{P}] dP$$

$$= T_0 R \ln \frac{P}{P^0}$$

Therefore,

$$(\beta_T)_{h,i} = 0.35 (1033.15 - 298.15)$$

$$= 257.3 \quad \text{kcal/kg}$$

$$(\beta_P)_{h,i} = 0$$

$$(\varepsilon_T)_{h,i} = 0.35 \left[(1033.15 - 298.15) - 298.15 \ \ln \frac{1033.15}{298.15} \right]$$

$$= 127.6 \ \text{kcal/kg}$$

$$(\varepsilon_P)_{h,i} = 0$$

$$(\beta_T)_{h,e} = 0.35 \ (853.15 - 298.15)$$

$$= 194.3 \ \text{kcal/kg}$$

$$(\beta_P)_{h,e} = 0$$

$$(\varepsilon_T)_{h,e} = 0.35 \left[(853.15 - 298.15) - 298.15 \ \ln \frac{853.15}{298.15} \right]$$

$$= 84.54 \ \text{kcal/kg}$$

$$(\varepsilon_P)_{h,e} = 298.15 \times \frac{1.987}{25.6} \ \ln \frac{1.079}{1}$$

$$= 1.760 \ \text{kcal/kg}$$

$$(\beta_T)_{c,i} = 0$$

$$(\beta_P)_{c,i} = 0$$

$$(\varepsilon_T)_{c,i} = 0$$

$$(\varepsilon_P)_{c,i} = 0$$

$$(\beta_T)_{c,e} = 0.25 \ (825.15 - 298.15)$$

$$= 131.8 \ \text{kcal/kg}$$

$$(\beta_P)_{c,e} = 0$$

$$(\varepsilon_T)_{c,e} = 0.25 \left[(825.15 - 298.15) - 298.15 \ \ln \frac{825.15}{298.15} \right]$$

$$= 55.37 \ \text{kcal/kg}$$

$$(\varepsilon_P)_{c,e} = 298.15 \times \frac{1.987}{29} \ \ln \frac{1.094}{1}$$

$$= 1.835 \ \text{kcal/kg}$$

By letting H_{av} and A_{ex} indicate the energy and available energy contents, respectively, we have

$$H_{av} = M(\beta^0 + \beta_T + \beta_P)$$

and

$$A_{ex} = M(\varepsilon^0 + \varepsilon_T + \varepsilon_P)$$

Therefore,

$$(H_{av})_{h,i} = 20,000 \ (147.2 + 257.3 + 0)$$

$$= 8,090,000 \ \text{kcal/hr}$$

$$(H_{av})_{h,e} = 20,000 \ (147.2 + 194.3 + 0)$$

$$= 6,830,000 \ \text{kcal/hr}$$

$$(H_{av})_{c,i} = 0$$

$$(H_{av})_{c,e} = 9,500 \ (0 + 131.8 + 0)$$

$$= 1,252,000 \ \text{kcal/hr}$$

$$(A_{ex})_{h,i} = 20,000 \ (45.93 + 127.6 + 0)$$

$$= 3,471,000 \ \text{kcal/hr}$$

$$(A_{ex})_{h,e} = 20,000 \ (45.93 + 84.54 + 1.760)$$

$$= 2,645,000 \ \text{kcal/hr}$$

$$(A_{ex})_{c,i} = 0$$

$$(A_{ex})_{c,e} = 9,500 \ (0 + 53.87 + 1.835)$$

$$= 548,200 \ \text{kcal/hr}$$

Therefore, from the energy balance of the system, the energy loss from the walls of the system to the environment is

$$[|Q_0| + |(W_x)_0|] = [(H_{av})_{h,i} + (H_{av})_{c,i}] - [(H_{av})_{h,e} + (H_{av})_{c,e}]$$

$$+ |W_{P1}| + |W_{P2}|$$

$$= (8,090,000 + 0) - (6,830,000 + 1,252,000)$$

$$+ 44,100 + 18,500$$

$$= 70,600 \text{ kcal/hr}$$

From the available energy balance of the system, the available energy dissipation is

$$[(T_0\sigma) + |(W_x)_0|] = [(A_{ex})_{h,i} + (A_{ex})_{c,i}] - [(A_{ex})_{h,e} + (A_{ex})_{c,e}]$$

$$+ |W_{P1}| + |W_{P2}|$$

$$= (3,471,000 + 0) - (2,645,000 + 548,200)$$

$$+ 44,100 + 18,500$$

$$= 340,400 \text{ kcal/hr}$$

For the case where both stream outputs are not exhausted to the environment, i.e., operating mode P1, the mass utilization efficiency, $(\eta_m)_{P1}$, and the thermodynamic first-law and second-law process efficiencies, $(\eta_1)_{P1}$ and $(\eta_2)_{P1}$, can be calculated from equations (52) through (54) as

$$(\eta_m)_{P1} = \frac{20,000 + 9,500}{20,000 + 9,500} \times 100$$

$$= 100\%$$

$$(\eta_1)_{P1} = \frac{6,830,000 + 1,252,000}{8,090,000 + 0 + 44,100 + 18,500} \times 100$$

$$= 99.13\%$$

$$(\eta_2)_{P1} = \frac{2,645,000 + 548,000}{3,471,000 + 0 + 44,100 + 18,500} \times 100$$

$$= 90.37\%$$

For operating mode P1, the mass, energy and available energy flow diagrams for the counter-current heat exchanger under consideration are shown in Figs. 2, 3, and 4, respectively. Similarly, for operating mode P2 where only the hot-stream output is usable, we have

$$(\eta_m)_{P2} = 67.80\%$$

$$(\eta_1)_{P2} = 83.78\%$$

$$(\eta_2)_{P2} = 74.85\%$$

and for operating mode P3 where only the cold-stream output is usable, we have

$$(\eta_m)_{P3} = 32.20\%$$

$$(\eta_1)_{P3} = 15.36\%$$

$$(\eta_2)_{P3} = 15.52\%$$

The thermodynamic first-law and second-law incremental efficiencies can be calculated by equations (55) and (56) as

$$(\eta_1^-)_D = \frac{(1,252,000 - 0)}{(8,090,000 - 6,830,000) + 44,100 + 18,500} \times 100$$

$$= 94.66\%$$

$$(\eta_2)_D = \frac{(548,200 - 0)}{(3,471,000 - 2,645,000) + 44,100 + 18,500} \times 100$$

$$= 61.69\%$$

NOMENCLATURE

A_{ex} = available energy, J or kcal

c_p = specific heat at constant pressure, J/kmol·K or J/kg·K

H_{av} = energy, J or kcal

h = molar enthalpy, J/kmol

M = mass flow rate, kg/sec or kg/hr

Mw = molecular weight, kg/kmol

n = molar flow rate including both the convective and diffusional flows, kmol/sec or kmol/hr

P = pressure, atm

Q_0 = heat loss from the system per unit time, J/sec or kcal/hr

s = molar entropy, J/kmol

T = temperature, K

v = specific volume, m^3/kg

$|W|$ = work per unit time, J/sec or kcal/hr

$|(W_x)_0|$ = work loss to the environment except that due to the expansion of the boundaries of the system per unit time, J/sec or kcal/hr

GREEK

β = enthalpy relative to the dead state per unit mole or mass, J/kmol or kcal/kg

β^0 = chemical enthalpy per unit mole or mass, J/kmol or kcal/kg

β_P = pressure enthalpy per unit mole or mass, J/kmol or kcal/kg

β_T = thermal enthalpy per unit mole or mass, J/kmol or kcal/kg

γ = entropy relative to the dead state per unit mole or mass, J/kmol·K or kcal/kg·K

γ^0 = chemical entropy per unit mole or mass, J/kmol·K or kcal/kg·K

γ_p = pressure entropy per unit mole or mass, J/kmol·K or kcal/kg·K

γ_T = thermal entropy per unit mole or mass, J/kmol·K or kcal/kg·K

ε = exergy per unit mole or mass, J/kmol or kcal/kg

ε^0 = chemical exergy per unit mole or mass, J/kmol or kcal/kg

ε_P = pressure exergy per unit mole or mass, J/kmol or kcal/kg

ε_T = thermal exergy per unit mole or mass, J/kmol or kcal/kg

η_m = mass utilization efficientcy

$(\eta_1)_D$ = thermodynamic first-law incremental efficiency

$(\eta_1)_P$ = thermodynamic first-law process efficiency

$(\eta_2)_D$ = thermodynamic second-law incremental efficiency

$(\eta_2)_P$ = thermodynamic second-law process efficiency

σ = created entropy per unit time, J/K·sec or kcal/K·hr

SUBSCRIPTS

0 = dead state

c = cold stream

e = outlet

h = hot stream

i = inlet

ℓ = leakage

P1 = pump or blower P1

P2 = pump or blower P2

SUPERSCRIPTS

0 = standard state

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Fig. 1. Counter-current heat exchanger.

Total Input
[100]

(Cold)$_i$
[32.20]

(Hot)$_i$
[67.80]

(Cold)$_e$
(32.20)

(Hot)$_e$
(67.80)

Total Output
(100)
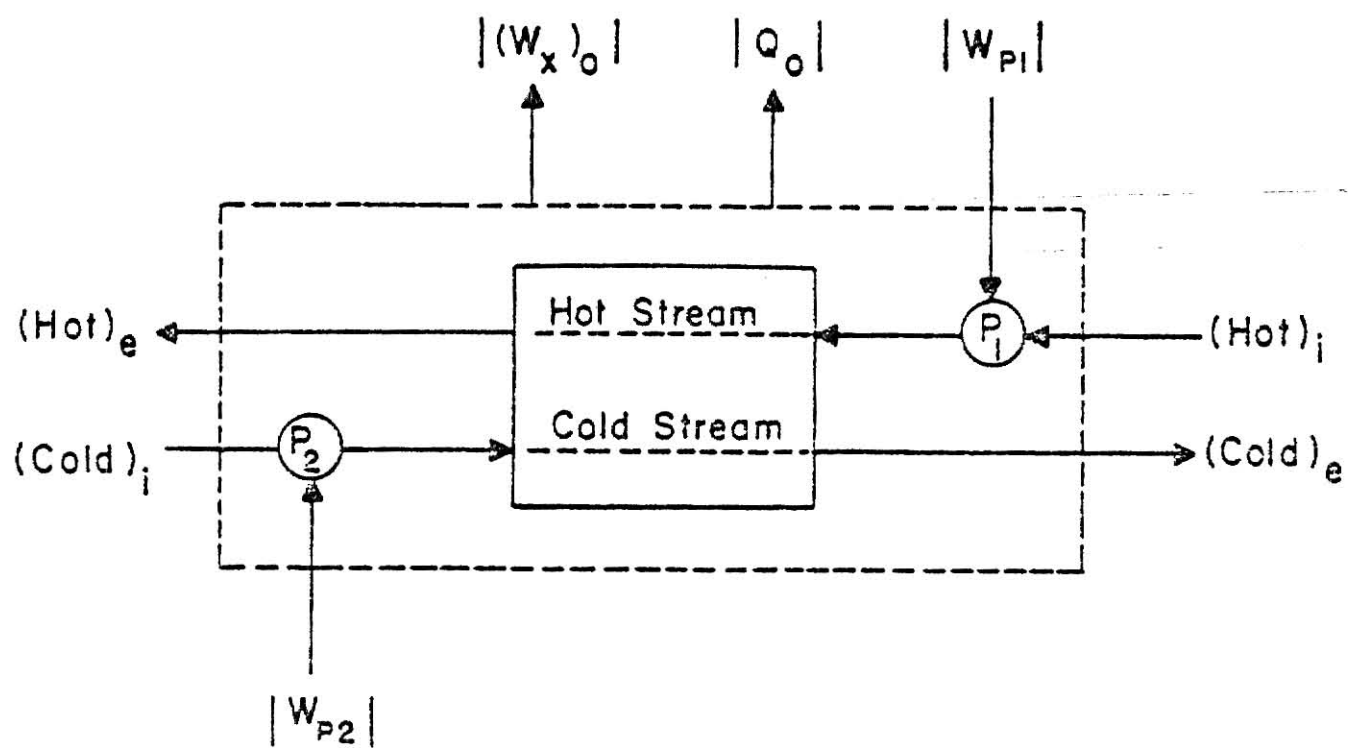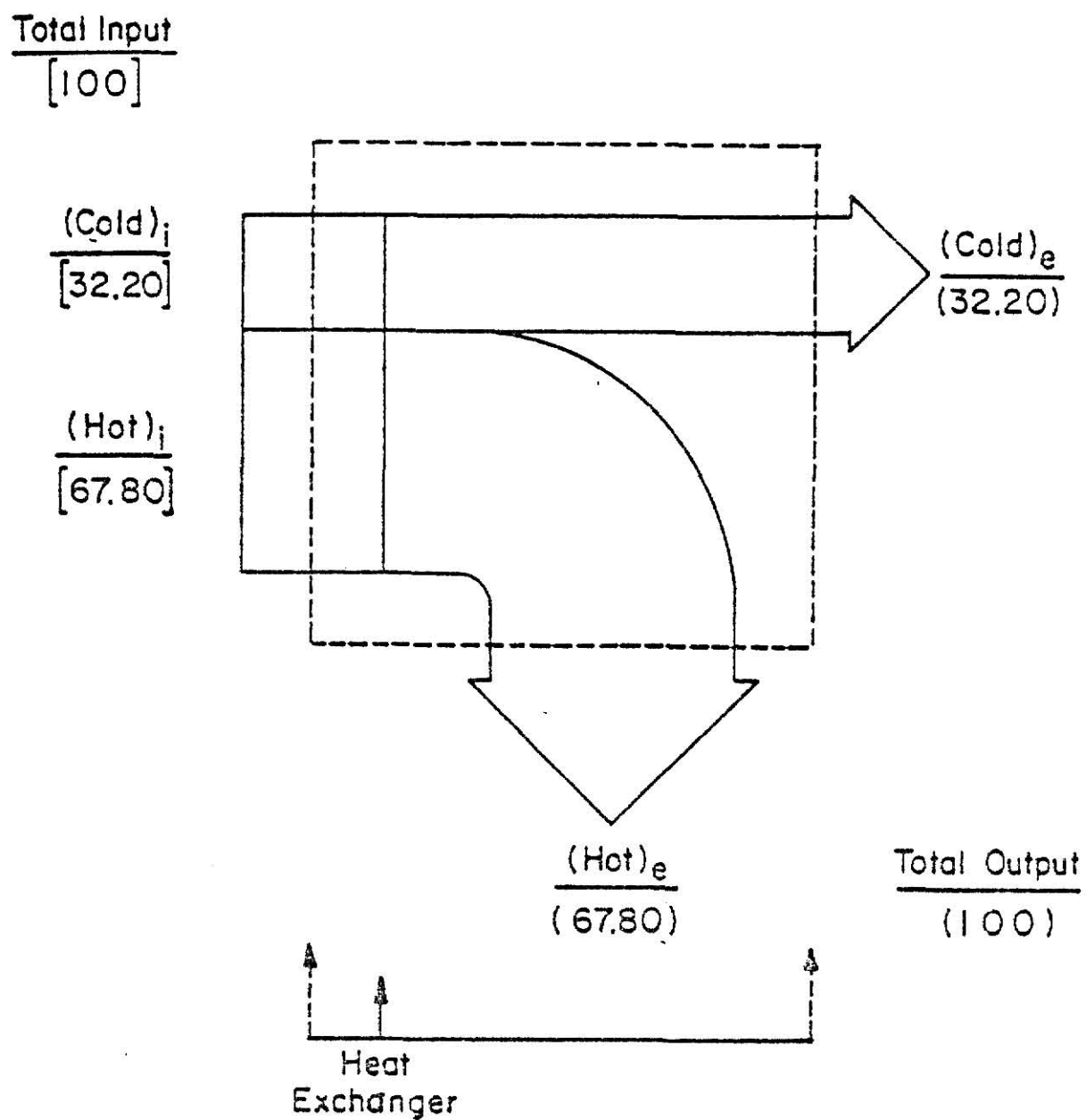
Heat
Exchanger

Fig. 2. Mass flow diagram for the
heat exchanger system.
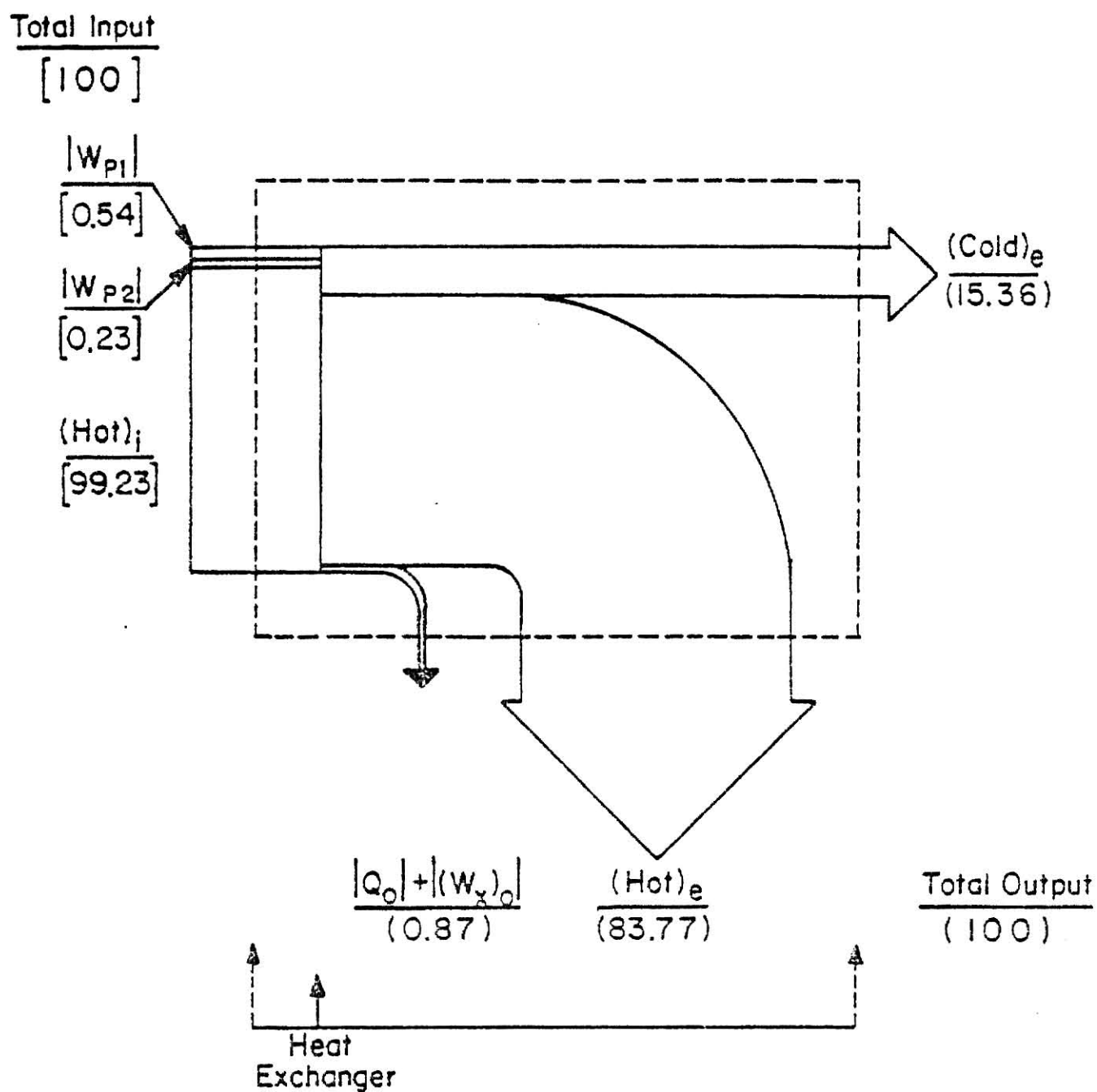
Fig. 3. Energy flow diagram for the heat exchanger system.
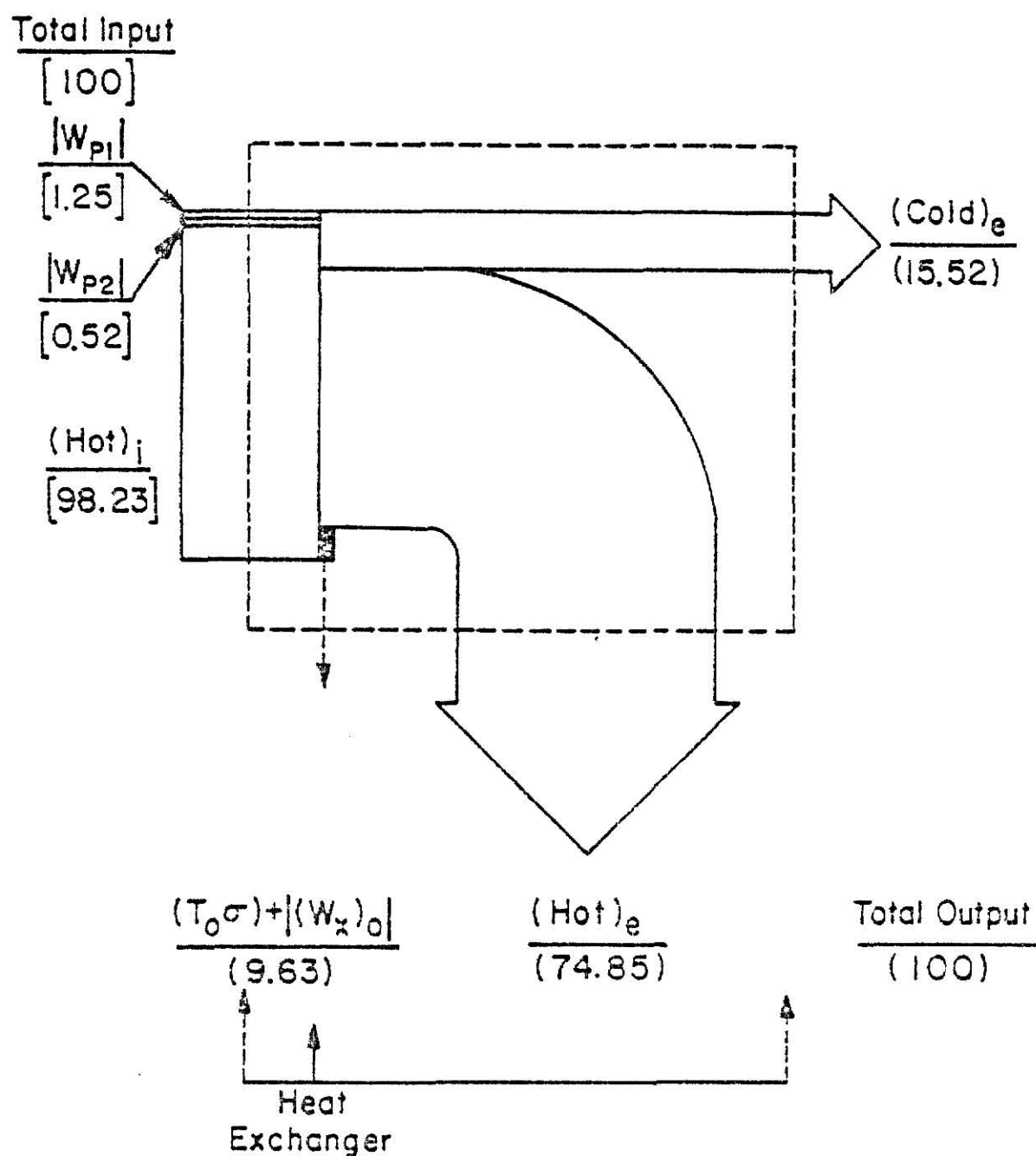
Fig. 4. Available energy flow diagram for the
heat exchanger system.

CHAPTER 5

THERMODYNAMIC ANALYSIS OF

A BIOMASS PYROLYSIS PROCESS

THERMODYNAMIC ANALYSIS OF
A BIOMASS PYROLYSIS PROCESS

A great deal of effort has been devoted to the development of processes for utilizing biomass as an energy source because of the continual decline in the availability of natural resources. The biomass pyrolysis system under consideration consists of a pyrolizer and a burner-boiler; it recovers energy from refuse by producing steam.

Several articles have been published dealing with energy conservation in the pyrolysis process. Lewis (1976) discussed several configurations of the process and made comparative analysis based on the material and energy balances. Otoma and Gotoh (1979) applied the second law of thermodynamics for analyzing the system. Recently, formulas for estimating more precisely the energy and available energy contents of structurally complicated materials, such as coal and biomass, have been developed (Shieh and Fan, 1982); these formulas are useful for analyzing process systems, e.g., the pyrolysis system under consideration, based on the first and second laws of thermodynamics.

The purposes of this chapter are:

1. to establish the rigorous mass, energy and available energy balances for the pyrolysis system by taking into account the material leakage, energy loss and available energy dissipation from the system to the surroundings,

2. to evaluate the thermodynamic first-law and second-law efficiencies of the system, based consistently on the balances, and

3. to identify sources of thermodynamic inefficiency in
    the system indicated by the balances and efficiencies,
    and to propose some possible means for reducing or
    eliminating such sources of inefficiencies.

For convenience, some of the governing equations for this system analysis,
derived in Chapter 3, are repeated in the succeeding section.

THERMODYNAMIC BACKGROUND

For ease of presentation and convenience, let us visualize a system shown in Fig. 1. This overall system contains several systems including system A, which is a steady-state open flow system with multiple input and output streams, system M1, a heat source at temperature T_{m1}, system M2, a heat sink at temperature T_{m2}, system N1, a work source, system N2, a work sink, and even the environment surrounding all these systems, D. As the preliminaries to the present work, equations of the mass, energy, entropy and available energy balances around the open flow system of our concern, system A, in Fig. 1 are presented as well as the definition of the mass utilization efficiency and those of the thermodynamic first-law and second-law efficiencies of the system (see, e.g., Keenen 1941, 1951; Rant, 1956; Denbigh, 1956, 1971; Szargut and Petela, 1965; Evans, 1969, 1980; Riekert, 1974; Gaggioli and Petit, 1977; Fan and Shieh 1980; Fan et al., 1982). Since we are concerned with a steady-state flow system, all the resultant balances are independent of time. For convenience, however, all the terms involved in these balances are considered to be on the unit time basis.

Mass Balance

Application of the law of mass conservation to system A leads to

$$\sum_{i}\left[\sum_{k}(Mw)_k n_k\right]_i = \sum_{e}\left[\sum_{k}(Mw)_k n_k\right]_e + \sum_{\ell}\left[\sum_{k}(Mw)_k n_k\right]_\ell \tag{1}$$

where

  Mw = molecular weight

  n = molar flow rate through the system including both the convective and diffusional flows at the inlet or exit of system A

  k = subscript designating material species

  i = subscript designating the inlet

  e = subscript designating the exit

  ℓ = subscript designating leakage

It is not uncommon that one or more of the exit streams are discarded because they contain by-products considered to be useless or wastes. Therefore, equation (1) can be conveniently rewritten as

$$\Sigma M_i = \Sigma M_{e,u} + \Sigma M_{e,d} + \Sigma M_\ell \tag{2}$$

In this expression, the left hand side, ΣM_i, is the overall input of mass, corresponding to the left hand side of equation (1); the first and second terms of the right hand side, $\Sigma M_{e,u}$ and $\Sigma M_{e,d}$, are the usable and discarded parts of the mass output, respectively, collectively corresponding to the first term of the right hand side of equation (1); and the third term, ΣM_ℓ, is the leakage, corresponding to the second term of the right hand side of equation (1).

Energy Balance

Applying the first law of thermodynamics to system A and assuming that potential energy, kinetic energy, etc. are negligible, we have

$$[\sum_i (\sum_k \overline{\beta}_k n_k)_i + |Q_1| + |W_1|]$$

$$= [\sum_e (\sum_k \overline{\beta}_k n_k)_e + |Q_2| + |W_2|] + [\sum_\ell (\sum_k \overline{\beta}_k n_k)_\ell]$$

$$+ [|Q_0| + |(W_x)_0|] \tag{3}$$

where

$|Q_1|$ = heat transmitted from system M1 to system A

$|Q_2|$ = heat transmitted from system A to system M2

$|Q_0|$ = heat loss from system A to the surroundings

$|W_1|$ = work supplied from system N1 to system A

$|W_2|$ = work supplied from system A to system N2

$|(W_x)_0|$ = work loss to the surroundings excluding that due to the expansion of the boundaries of system A

$\overline{\beta}$ = partial molar enthalpy relative to the dead state

$\overline{\beta}$ is defined as (see, e.g., Szargut and Petela, 1965; Rodriguez, 1980; Fan and Shieh, 1980)

$$\overline{\beta} \equiv \overline{h} - \overline{h}_0, \tag{4}$$

and thus, it can be written

$$\overline{\beta} = \overline{h} - \overline{h}^0 + \overline{h}^0 - \overline{h}_0$$

$$= (\overline{h}^0 - \overline{h}_0) + [\int_{T^0}^{T} (\frac{\partial \overline{h}}{\partial T})_P dT + \int_{P^0}^{P} (\frac{\partial \overline{h}}{\partial P})_T dP]$$

$$= \overline{\beta}^0 + [\int_{T^0}^{T} (\frac{\partial \overline{h}}{\partial T})_P dT + \int_{P^0}^{P} (\frac{\partial \overline{h}}{\partial P})_T dP] \tag{5}$$

where

$$\overline{\beta}^0 \equiv \overline{h}^0 - \overline{h}_0 \tag{6}$$

From the definition of $\overline{h}$ and the Maxwell relationship, equation (5) can be rewritten as

$$\overline{\beta} = \overline{\beta}^0 + \int_{T^0}^{T} \overline{c}_P dT + \int_{P^0}^{P} [\overline{v} - T(\frac{\partial \overline{v}}{\partial T})_P] dP \tag{7}$$

where superscript 0 refers to the standard state and subscript 0 to the dead state; $\overline{\beta}^0$ may be named the partial molar chemical enthalpy.

When one or more of the exit streams are discarded to the environment as wastes, equation (3) can be conveniently expressed as

$$[\Sigma(H_{av})_i] = [\Sigma(H_{av})_{e,u} + \Sigma(H_{av})_{e,d}] + [\Sigma(H_{av})_\ell] + [\Sigma(H_{av})_c] \tag{8}$$

The left hand side, $\Sigma(H_{av})_i$, in this equation is the total energy input in forms of enthalpy, heat and work; the first term of the right hand side, $\Sigma(H_{av})_{e,u}$, the usable portion of the energy output in forms of enthalpy, heat and work; the second term, $\Sigma(H_{av})_{e,d}$, the portion of the energy output associated with the discarded material streams; the third

term, $\Sigma(H_{av})_\ell$, the energy associated with the material leakage; and the last term, $\Sigma(H_{av})_c$, the energy consumption which consists of heat loss through the wall, $|Q_0|$, and the work loss, $|(W_x)_0|$. There exists a one-to-one correspondence between the equivalent terms in equations (3) and (8), all bracketed by [ ].

Suppose that i_1 number of the inlet streams can be identified as the streams which lose their enthalpy contents to become e_1 number of the exit streams, and ℓ_1 number of the leakage streams, and i_2 number of the inlet streams as the streams which gain their enthalpy contents to become e_2 number of the exit streams and ℓ_2 number of the leakage streams during their passage through system A. Then, equation (3) becomes

$$\left\{\left[\sum_{i_1}(\sum_k \bar{\beta}_k n_k)_{i_1} + \sum_{i_2}(\sum_k \bar{\beta}_k n_k)_{i_2}\right] + |Q_1| + |W_1|\right\}$$

$$= \left\{\left[\sum_{e_1}(\sum_k \bar{\beta}_k n_k)_{e_1} + \sum_{e_2}(\sum_k \bar{\beta}_k n_k)_{e_2}\right] + |Q_2| + |W_2|\right\}$$

$$+ \left\{\left[\sum_{\ell_1}(\sum_k \bar{\beta}_k n_k)_{\ell_1} + \sum_{\ell_2}(\sum_k \bar{\beta}_k n_k)_{\ell_2} + |Q_0| + |(W_x)_0|\right\}\right. \tag{9}$$

Since the separately identifiable material streams act either as energy sinks or as energy sources to system A, it is often convenient to rewrite this equation, by grouping the corresponding terms, as

$$\left\{\left[\sum_{i_1}(\sum_k \bar{\beta}_k n_k)_{i_1} - \sum_{e_1}(\sum_k \bar{\beta}_k n_k)_{e_1} - \sum_{\ell_1}(\sum_k \bar{\beta}_k n_k)_{\ell_1}\right] + \left[|Q_1| + |W_1|\right]\right\}$$

$$= \left\{\left[\sum_{e_2}(\sum_k \bar{\beta}_k n_k)_{e_2} + \sum_{\ell_2}(\sum_k \bar{\beta}_k n_k)_{\ell_2} - \sum_{i_2}(\sum_k \bar{\beta}_k n_k)_{i_2}\right] + \left[|Q_2| + |W_2|\right]\right\}$$

$$+ \left\{|Q_0| + |(W_x)_0|\right\} \tag{10}$$

This equation can be rewritten as

$$\{\Sigma(H_{av})_i\}_D = \{\Sigma(H_{av})_e\}_D + \{\Sigma(H_{av})_c\} \tag{11}$$

where $\{\Sigma(H_{av})_i\}_D$ is the energy transferred to system A from the energy sources, including heat sources, work sources and process streams which lose energy contents during their passage through the system, $\{\Sigma(H_{av})_e\}_D$ is the energy transferred by system A to the energy sinks, including heat sinks, work sinks and process streams which gain energy contents during their passage through the system, and $\{\Sigma(H_{av})_c\}$ is the energy consumption due to the loss through the walls of system A. In other words, there exists a one-to-one correspondence between the equivalent terms in equations (10) and (11), all grouped by brackets, { }.

Entropy Balance

The entire system shown in Fig. 1, including the surroundings, is isolated; thus, the statement of the second law of thermodynamics can be expressed as

$$\sum_i(\sum_k \bar{\gamma}_k n_k)_i + \frac{|Q_1|}{T_{m1}}$$

$$= \sum_e(\sum_k \bar{\gamma}_k n_k)_e + \sum_\ell(\sum_k \bar{\gamma}_k n_k)_\ell + \frac{|Q_2|}{T_{m2}} + \frac{|Q_0|}{T_0} - \sigma \tag{12}$$

where σ is the created entropy or entropy generation in the system and $\bar{\gamma}$ is the partial molar entropy relative to the dead state; it is defined as (see, e.g., Szargut and Petela, 1965; Fan and Shieh, 1980)

$$\bar{\gamma} \equiv \bar{s} - \bar{s}_0,$$

and thus, it can be written as

$$\overline{\gamma} = \overline{s} - \overline{s}^0 + \overline{s}^0 - \overline{s}_0$$

$$= (\overline{s}^0 - \overline{s}_0^-) + [\int_{T^0}^{T} (\frac{\partial \overline{s}}{\partial T})_P \, dT + \int_{P^0}^{P} (\frac{\partial \overline{s}}{\partial P})_T \, dP] \tag{14}$$

By letting

$$\overline{\gamma}^0 \equiv \overline{s}^0 - \overline{s}_0 \tag{15}$$

and applying the definition of $\overline{s}$ and the Maxwell relationship to equation (14), we have

$$\overline{\gamma} = \overline{\gamma}^0 + \int_{T^0}^{T} \frac{\overline{c}_P}{T} \, dT - \int_{P^0}^{P} (\frac{\partial \overline{v}}{\partial T})_P \, dP \tag{16}$$

where $\overline{\gamma}^0$ may be called partial molar chemical entropy.

Available Energy Balance

Combination of the energy balance, equation (3), and the entropy balance, equation (12), gives rise to

$$[\sum_i (\sum_k \overline{\epsilon}_k n_k)_i + |Q_1|(1 - \frac{T_0}{T_{m1}}) + |W_1|]$$

$$= [\sum_e (\sum_k \overline{\epsilon}_k n_k)_e + |Q_2|(1 - \frac{T_0}{T_{m2}}) + |W_2|] + [\sum_\ell (\sum_k \overline{\epsilon}_k n_k)_\ell]$$

$$+ [|(W_x)_0| + (T_0\sigma)] \tag{17}$$

where $\overline{\epsilon}$ is the partial molar exergy and is defined as (see, e.g., Gaggioli, 1961; Szargut and Petela, 1965; Riekert, 1974; Fan and Shieh, 1980)

$$\overline{\epsilon} \equiv (\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0), \tag{18}$$

and thus, this equation can be transformed as

$$\overline{\epsilon} = \overline{\beta} - T_0\overline{\gamma}$$

$$= (\overline{\beta}^0 - T_0\overline{\gamma}^0) + \int_{T^0}^{T} \overline{c}_P (1 - \frac{T_0}{T}) \, dT$$

$$+ \int_{P^0}^{P} [\overline{v} - (T - T_0) (\frac{\partial \overline{v}}{\partial T})_P] \, dP \tag{19}$$

By letting

$$\overline{\epsilon}^0 \equiv \overline{\beta}^0 - T_0\overline{\gamma}^0 , \tag{20}$$

we have

$$\overline{\epsilon} = \overline{\epsilon}^0 + \int_{T^0}^{T} \overline{c}_P (1 - \frac{T_0}{T}) \, dT$$

$$+ \int_{P^0}^{P} [\overline{v} - (T - T_0) (\frac{\partial \overline{v}}{\partial T})_P] \, dP \tag{21}$$

where $\overline{\epsilon}^0$ may be named partial molar chemical exergy.

Similar to equation (8), equation (17) can be expressed as

$$[\Sigma(A_{ex})_i] = [\Sigma(A_{ex})_{e,u} + \Sigma(A_{ex})_{e,d}] + [\Sigma(A_{ex})_{\ell}] + [\Sigma(A_{ex})_{dis}] \tag{22}$$

where $\Sigma(A_{ex})_i$ is the total available energy input associated with the material streams, heat and work, $\Sigma(A_{ex})_{e,u}$ the usable portion of the available energy output associated with the material streams, heat and work, $\Sigma(A_{ex})_{e,d}$ the portion of the available energy output associated with the discarded material streams, $\Sigma(A_{ex})_{\ell}$ the available energy associated with the material leakage, and $\Sigma(A_{ex})_{dis}$ the available energy dissipation containing $|(W_x)_d|$ and $(T_0\sigma)$. All terms grouped by square brackets, [ ], in equation (22)

correspond in order to those in equation (17). Also similar to equations (10) and (11), it is often convenient to rewrite equation (17) as

$$\{[\sum_{i_1} (\sum_k \bar{\epsilon}_k n_k)_{i_1} - \sum_{e_1} (\sum_k \bar{\epsilon}_k n_k)_{e_1} - \sum_{\ell_1} (\sum_k \bar{\epsilon}_k n_k)_{\ell_1}]$$

$$+ [|Q_1| (1 - \frac{T_0}{T_{m1}}) + |W_1|]\}$$

$$= \{[\sum_{e_2} (\sum_k \bar{\epsilon}_k n_k)_{e_2} + \sum_{\ell_2} (\sum_k \bar{\epsilon}_k n_k)_{\ell_2} - \sum_{i_2} (\sum_k \bar{\epsilon}_k n_k)_{i_2}]$$

$$+ [|Q_2| (1 - \frac{T_0}{T_{m2}}) + |W_2|]\} + \{|(W_x)_0| + (T_0\sigma)\} \qquad (23)$$

and

$$\{\sum (A_{ex})_i\}_D = \{\sum (A_{ex})_e\}_D + \{\sum (A_{ex})_{dis}\} \qquad (24)$$

where $\{\sum (A_{ex})_i\}_D$ is the available energy transferred to system A from the energy sources, including heat sources, work sources and process streams which lose available energy contents during their passage through the system, $\{\sum (A_{ex})_e\}_D$ is the available energy transferred from system A to the energy sinks, including heat sinks, work sinks and process streams which gain available energy contents during their passage through the system, and $\{\sum (A_{ex})_{dis}\}$ is the available energy dissipation. In other words, all the terms grouped by brackets, { }, in equation (24) correspond in order to those in equaiton (23).

Thermodynamic Efficiencies

Qualitatively speaking, the efficiency of a system is the effectively utilized fraction of mass, energy, available energy or any other quantity or

commodity, which has been supplied to the system. From the thermodynamic point of view, three broad classes of efficiencies can be defined: they are the mass utilization efficiency and the first-law and second-law efficiencies.

From equation (2), the mass utilization efficiency can be expressed as

$$\eta_m = \frac{\Sigma\, M_{e,u}}{\Sigma\, M_i} \tag{25}$$

The first-law process and incremental (or extractive) efficiencies of a process system can be expressed from equations (8) and (11), respectively, as

$$(\eta_1)_P = \frac{[\Sigma (H_{av})_{e,u}]}{[\Sigma (H_{av})_i\ ]} \tag{26}$$

and

$$(\eta_1)_D = \frac{\{\Sigma (H_{av})_e\}_D}{\{\Sigma (H_{av})_i\}_D} \tag{27}$$

Similarly, the second-law process and incremental efficiencies can be expressed from equations (22) and (24), respectively, as

$$(\eta_2)_P = \frac{[\Sigma (A_{ex})_{e,u}]}{[\Sigma (A_{ex})_i\ ]} \tag{28}$$

$$(\eta_2)_D = \frac{\{\Sigma (A_{ex})_e\}_D}{\{\Sigma (A_{ex})_i\}_D} \tag{29}$$

The thermodynamic process efficiency, as defined by equation (26) or (28), is mainly concerned with the conservation of energy or available energy. In contrast, the thermodynamic incremental efficiency, as defined by equation (27) or (29),is mainly concerned with the transformation of energy or available energy.

COMPUTATIONAL PROCEDURE

Equations (2), (8), (11), (22) and (24) indicate that, broadly speaking, the causes of thermal inefficiency are: (a) energy loss from the walls of the system to the surroundings, $[\Sigma(H_{av})_c]$, (b) available energy dissipation due to all types of irreversibilities, $[\Sigma(A_{ex})_{dis}]$, (c) combined effect of the energy loss associated with the discarded material streams and the material leakage, and that from the walls of the system to the surroundings, $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_\ell + \Sigma(H_{av})_c]$, and (d) combined effect of the available energy loss associated with the discarded material streams and the material leakage, and the available energy dissipation due to all types of irreversibilities, $[\Sigma(A_{ex})_{e,d} + \Sigma(A_{ex})_\ell + \Sigma(A_{ex})_{dis}]$.

Explicit inclusion of the expression for the mass balance, equation (2), and that for the mass utilization efficiency, equation (25), in the present approach has been prompted by the fact that the material wastage and leakage can affect drastically and negatively the thermo-dynamic efficiencies of the process system as indicated by equations (26) through (29). Furthermore, $[\Sigma(H_{av})_c]$ is imbedded in $[\Sigma(A_{ex})_{dis}]$ and $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_\ell + \Sigma(H_{av})_c]$, and these quantities, in turn, are imbedded in $[\Sigma(A_{ex})_{e,d} + \Sigma(A_{ex})_\ell + \Sigma(A_{ex})_{dis}]$. Thus, the principle of optimality (Bellman, 1957) indicates that a logical sequence exists for thermodynamically analyzing a process system to identify the nature and sources of thermodynamic inefficiencies. The sequence is as follows:

Step 1. Evaluation of the material wastage, $\Sigma M_{e,d}$, and the material leakage, ΣM_ℓ, by equation (2) and the mass utilization efficiency, η_m, by equation (25).

Step 2. Evaluation of the energy consumption, $[\Sigma(H_{av})_c]$, and

the first-law incremental efficiency, $(\eta_1)_D$, by equations

(11) and (27), respectively.

Step 3. Evaluation of the available energy dissipation, $[\Sigma(A_{ex})_{dis}]$,

and the second-law incremental efficiency, $(\eta_2)_D$, by

equations (24) and (29), respectively.

Step 4. Evaluation of the energy loss, $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_\ell$

$+ \Sigma(H_{av})_c]$, and the first-law process efficiency,

$(\eta_1)_P$, by equations (8) and (26), respectively.

Step 5. Evaluation of the available energy loss, $[\Sigma(A_{ex})_{e,d}$

$+ \Sigma(A_{ex})_\ell + \Sigma(A_{ex})_{dis}]$, and the second-law process efficiency,

$(\eta_2)_P$, by equations (22) and (28), respectivley.

The results will indicate the possible remedial measures for reducing
or eliminating the sources of thermodynamic inefficiencies identified.
The large values of $[\Sigma(H_{av})_c]$ and $[\Sigma(A_{ex})_{dis}]$ tend to give rise to low
first-law and second-law incremental efficiencies, respectively, and
the large values of $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_\ell + \Sigma(H_{av})_c]$ and $[\Sigma(A_{ex})_{e,d} + \Sigma(A_{ex})_\ell$
$+ \Sigma(A_{ex})_{dis}]$ tend to yield low first-law and second-law process
efficiencies, respectively.

PROCESS DESCRIPTION

The process under consideration consists of three subsystems, namely the pyrolizer, the pump, and the burner and boiler as shown in Fig. 2. This process is fed with 1,000 kg/hr (2,205 lb/hr) of refuse to generate 1,772 kg/hr (3,907 lb/hr) of steam which is used for power generation (see, e.g., Kaiser and Friedman, 1967; Lewis, 1976; Otoma and Gotoh, 1980).

Pyrolizer subsystem

The pyrolizer is of the indirectly heated and rotary kiln type. The refuse, which is composed of carbon, hydrogen, oxygen, moisture and ash, is fed into the pyrolizer to produce char, which is discharged at 1,033.15 K (1,860° R), and pyrolysis gas. A portion of the pyrolysis gas is burnt in the pyrolizer to maintain its temperature. The remainder of the pyrolysis gas together with the exhaust from the fire box of the pyrolizer is the product gas at 1,033.15 K (1,860°R) which is used as fuel gas in the burner and boiler subsystem. The compositions of the refuse and the char assumed here are shown in Table 1 and the components and their concentrations of the product gas in Table 2.

Pump, and Burner and Boiler Subsystems

The pump subsystem consumes 1.45×10^3 kcal/hr (1.686 kwh/hr) of energy to compress water from 1 atm (14.7 psia) to 25 atm (367.5 psia), and supplies the high pressure water into the burner and boiler subsystem.

In the burner and boiler subsystem, the product gas mixed with air is combusted to generate steam at 533.15 K (960° R) and 20 atm (294 psia). Flue gas, whose components and their concentrations are tabulated in Table 2, is discharged at 533.15 K (960° R).

Operating Modes

In this work, four operating modes are conceived for the biomass pyrolysis system under consideration. They are the following:

Mode P1. Steam is recovered as the only useful product from the entire system.

Mode P2. Steam and flue gas are recovered as useful products from the entire system.

Mode P3. Steam and char are recovered as useful products from the entire system.

Mode P4. All the products are recovered as useful products from the entire system.

RESULTS AND DISCUSSION

Computational results are presented in Tables 1 through 4. Table 1 gives the compositions, the specific chemical enthalpies, β^0, and the specific chemical exergies, ε^0, of the refuse and char (Fan and Shieh, 1982). In Table 2 the components and their concentrations, and the specific chemical enthalpies and exergies for the product gas and the flue gas are listed. Table 3 gives the flow rate, temperature, pressure, enthalpy relative to the dead state and exergy of each process stream, and work requirement. Table 4 contains the energy consumptions, $[\Sigma(H_{av})_c]$, their percentage contributions to the total energy consumption, the available energy dissipations, $[\Sigma(A_{ex})_{dis}]$, their percentage contributions to the total available energy dissipation and the thermodynamic first-law and second-law process and incremental efficiencies of each subsystem and the overall system for the four operating modes, P1, P2, P3 and P4.

As a whole, the biomass pyrolysis system under consideration requires 1,000 kg/hr (2,205 lb/hr) of refuse, which has $2,583 \times 10^3$ kcal/hr ($10,812 \times 10^3$ kJ/hr or $10,247 \times 10^3$ Btu/hr) of energy and $2,685 \times 10^3$ kcal/hr ($11,242 \times 10^3$ kJ/hr or $10,654 \times 10^3$ Btu/hr) of available energy, and loses 108.1×10^3 kcal/hr (452.3×10^3 kJ/hr or 428.7×10^3 Btu/hr) of energy from the walls of the system to the surroundings and $1,372 \times 10^3$ kcal/hr ($5,741 \times 10^3$ kJ/hr or $5,441 \times 10^3$ Btu/hr) of available energy due to all kinds of irreversibility. This system produces steam at a rate of 1,772 kg/hr (3,907 lb/hr), which has $1,196 \times 10^3$ kcal/hr ($5,006 \times 10^3$ kJ/hr or $4,744 \times 10^3$ Btu/hr) of energy and 409.12×10^3 kcal/hr ($1,713 \times 10^3$ kJ/hr or $1,623 \times 10^3$ Btu/hr) of available energy. Figures 3, 4 and 5 illustrate the mass, energy and available energy flow diagrams, respectively, for operating mode P4 of the system.

Energy Consumption, $[\Sigma(H_{av}{}_c)]$, and First-Law Incremental Efficiency, $(\eta_1)_D$

Table 4 in conjunction with Fig. 4 indicates that the pyrolizer sub-system consumes the largest amount of energy , 101.65×10^3 kcal/hr (94.06% of the total energy consumption). However, this amount of energy consumption is relatively small compared with energy entering this subsystem, i.e., 3.93% of the energy input as shown in Fig. 4. Furthermore, the energy consumption in either the pump subsystem or the burner and boiler subsystem is much less than that in the pyrolizer subsystem. Therefore, only a slight improvement in the first-law incremental efficiency of the overall system can be attained from enhancing the insulation to reduce the energy consumption.

As no process stream gains energy contents in the pyrolizer sub-system, it is not meaningful to identify the thermodynamic first-law incremental efficiency, $(\eta_1)_D$, for this subsystem. The thermodynamic first-law incremental efficiencies of the pump subsystem, the burner and boiler subsystem and the overall system are 71.12%, 99.50% and 91.71%, respectively.

Available Energy Dissipation, $\Sigma(A_{ex})_{dis}$, and Second-Law Incremental Efficiency, $(\eta_2)_D$

The available energy dissipations in the burner and boiler subsystem and the pyrolizer subsystem are substantial as indicated in Table 4 and Fig. 5. Quantitatively speaking, the burner and boiler subsystem dissipates the largest amount of available energy, 703.16×10^3 kcal/hr (51.24% of the total available energy dissipation), which corresponds to 26.17% of the total available energy entering the system. This gives rise to the rather low second-law incremental efficiency of 36.72%. The pyrolizer subsystem dissipates available energy at a rate of

668.78×10^3 kcal/hr (48.73% of the total available energy dissipated), cor-
responding to 24.89% of the total available energy entering the system. In
contrast, the available energy dissipation in the pump subsystem is negligib-
ly small, which leads to the relatively high second-law incremental efficiency
of 71.12%. The second-law incremental efficiency of the overall system is
22.97%.

As mentioned previously and also shown in Table 4 and Fig. 4, the amount
of energy consumption in the burner and boiler subsystem and that in the
pyrolizer subsystem are relatively small compared with the energy input to
the system. Therefore, the available energy dissipation in both the sub-
systems is mainly due to internal irreversibility, as expected from the nature
of the processes occurring in both the subsystems. A possible way to reduce the
internal irreversibility is to change the operating conditions and/or to
modify the process equipment employed in these subsystems.

Energy Loss, $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_c]$, and First-Law Process Efficiency, $(\eta_1)_p$

Table 4 gives the first-law process efficiencies of the subsystems
and the overall system, calculated for the four operating modes, P1, P2, P3
and P4. The char is discarded from the pyrolizer subsystem to the environ-
ment in the operating modes, P1 and P2. In these operating modes, the
pyrolizer subsystem loses the largest amount of energy, at a rate of
838.40×10^3 kcal/hr (32.83% of the total energy input), which leads to the
lowest first-law process efficiency of 67.54%, which is $(\eta_1)_{P1}$ or $(\eta_1)_{P2}$ in
Table 4. Note that 87.88% of this loss is the energy associated with
the discarded char, and the rest represents the heat loss from the wall
which is relatively small. Obviously, to improve this first-law process
efficiency, the char should be recovered to the maximum extent possi-
ble. With the char recovered in the operating modes, P3 and P4,

the first-law process efficiency of the pyrolizer subsystem is elevated to 96.06%, which is $(\eta_1)_{P3}$ or $(\eta_1)_{P4}$ in Table 4. As expected, the energy loss from the pump subsystem, which has the first-law process efficiency of 71.72%, is negligibly small compared with other subsystems.

The flue gas is discarded from the burner and boiler subsystem in the operating modes, P1 and P3. In either of these modes, the energy loss from this subsystem, $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_c]$, is 549.8 x 10^3 kcal/hr (21.27% of the total energy input), leading to the first-law process efficiency of 68.50%, which is $(\eta_1)_{P1}$ or $(\eta_1)_{P3}$ in Table 4. In this case, the heat loss from the wall of this subsystem to the environment is negligibly small; specifically, it corresponds to 1.1% of the energy loss from this subsystem. Thus, to improve substantially the first-law process efficiency of this subsystem, the energy loss associated with the flue gas need be reduced. This can be accomplished by installing an energy recovery unit for the flue gas. If the steam and flue gas are utilized in the operating modes, P2 and P4, the first-law process efficiency of this subsystem is upgraded to 99.66%, which is $(\eta_1)_{P2}$ or $(\eta_1)_{P4}$ in Table 4.

For the overall system, the first-law process efficiencies, $(\eta_1)_{P1}$, $(\eta_1)_{P2}$, $(\eta_1)_{P3}$ and $(\eta_1)_{P4}$ corresponding to the four operating modes, P1, P2, P3 and P4, are 46.27%, 67.31%, 74.78% and 95.82%, respectively. Obviously, installing energy or material recovery units in the system automatically improves the first-law process efficiency for the entire system. In practice, however, this is counterbalanced by the increment of capital cost of the system. A trade-off analysis need be made for the detailed design.

Available Energy Loss, $[\Sigma(A_{ex})_{e,d} + \Sigma(A_{ex})_{dis}]$, and Second-Law Process

Efficiency, $(\eta_2)_P$

Table 4 lists the second-law process efficiencies for the subsystems and the overall system, calculated for the four operating modes, P1, P2, P3 and P4. The pyrolizer subsystem discards the char in the operating modes, P1 and P2. In these modes, the available energy associated with the discarded char and the available energy dissipation are, respectively, 740.22 x 10^3 kcal/hr and 668.78 x 10^3 kcal/hr. The former corresponds to 27.55% of the total available energy input, and the latter 24.89%. This implies that both $\Sigma(A_{ex})_{e,d}$ and $\Sigma(A_{ex})_{dis}$ need be reduced substantially to improve the second-law process efficiency in this subsystem. The way to reduce the available energy dissipation has been discussed earlier and the available energy loss associated with the char can be reduced by recovering it as a useful by-product. In the operating modes, P3 and P4, the char is recovered so that the second-law process efficiency of this subsystem is improved from 50.22% to 77.79%.

The burner and boiler subsystem dissipates the available energy at an appreciably high rate; $[\Sigma(A_{ex})_{dis}]$ of this subsystem is 703.16 x 10^3 kcal/hr, which corresponds to 26.17% of the total available energy input. In the operating modes, P1 and P3, the available energy loss associated with the discarded flue gas is 165.35 x 10^3 kcal/hr, corresponding to 6.15% of the total available energy input. Therefore, reducing the available energy dissipation, which has been discussed earlier, is more important. In the operating modes, P2 and P4, the flue gas is recovered so that the second-law process efficiency is increased from 32.02% to 44.96%.

For the entire system, the second-law process efficiencies, $(\eta_2)_{P1}$, $(\eta_2)_{P2}$, $(\eta_2)_{P3}$ and $(\eta_2)_{P4}$, corresponding to the four operating modes, P1, P2, P3 and P4, are 15.23%, 21.38%, 42.77% and 48.93%, respectively. It should be noted that around 50% of the available energy input to the entire system is dissipated due to all kinds of irreversibility.

CONCLUDING REMARKS

The biomass pyrolysis process has been systematically analyzed from the thermodynamic viewpoint. The energy loss, the available energy loss, and the thermodynamic first-law and second-law process and incremental efficiencies have been evaluated for the four operating modes of the system.

The second-law efficiency has been found to be appreciably lower than the first-law efficiency, indicating the necessity of including the available energy balance in process analysis and design. The process efficiency has been found to be substantially different from the incremental efficiency, indicating the necessity of considering both energy conservation and transformation in process analysis and design.

Recovering the energy associated with the char and flue gas is essential for improving the thermodynamic first-law process efficiency, while recovering the available energy of the char and reducing the available energy dissipation due to all kinds of irreversibility are essential for improving the thermodynamic second-law process efficiency. Approximately 50% of the available energy entering the system is dissipated due to the irreversibility. The extent of energy loss from the walls of the system to the surroundings is relatively small compared with the energy entering the system.

NOMENCLATURE

A $\quad$ = system A

$(A_{ex})_i$ $\quad$ = available energy input per unit time, J/sec or kcal/hr

$(A_{ex})_{dis}$ $\quad$ = available energy dissipation per unit time, J/sec or kcal/hr

$(A_{ex})_{e,d}$ $\quad$ = discarded portion of the available energy output per unit time, J/sec or kcal/hr

$(A_{ex})_{e,u}$ $\quad$ = usable portion of the available energy output per unit time, J/sec or kcal/hr

$(A_{ex})_\ell$ $\quad$ = available energy leakage per unit time, J/sec or kcal/hr

$\{(A_{ex})_e\}_D$ $\quad$ = available energy transferred from system A to energy sinks per unit time, J/sec or kcal/hr

$\{(A_{ex})_i\}_D$ $\quad$ = available energy transferred from energy sources to system A per unit time, J/sec or kcal/hr

e $\quad$ = output streams

$(H_{av})_c$ $\quad$ = energy consumption per unit time, J/sec or kcal/hr

$(H_{av})_{e,d}$ $\quad$ = discarded portion of the energy output per unit time, J/sec or kcal/hr

$(H_{av})_{e,u}$ $\quad$ = usable portion of the energy output per unit time, J/sec or kcal/hr

$(H_{av})_i$ $\quad$ = energy input per unit time, J/sec or kcal/hr

$(H_{av})_\ell$ $\quad$ = energy leakage per unit time, J/sec or kcal/hr

$\{(H_{av})_e\}_D$ $\quad$ = energy transferred from system A to energy sinks per unit time, J/sec or kcal/hr

$\{(H_{av})_i\}_D$ $\quad$ = energy transferred from energy sources to system A per unit time, J/sec or kcal/hr

$\overline{h}$ = partial molar enthalpy, J/kmol or kcal/kmol

$\overline{h}_0$ = partial molar enthalpy at the dead state, J/kmol or kcal/kmol

i = input streams

k = material species

ℓ = leakage

$M_{e,d}$ = discarded part of mass output per unit time, kg/sec or kg/hr

$M_{e,u}$ = usable part of mass output per unit time, kg/sec or kg/hr

M_i = mass input per unit time, kg/sec or kg/hr

M_ℓ = mass leakage per unit time, kg/sec or kg/hr

Mw = molecular weight, kg/kmol

n = molar flow rate including both convective and diffusional

flows, kmol/sec or kmol/hr

P = pressure, atm

$|Q_0|$ = heat loss to the environment per unit time, J/sec or kcal/hr

$|Q_1|$ = heat transmitted from system M1 to system A per unit time,

J/sec or kcal/hr

$|Q_2|$ = heat transmitted from system A to system M2 per unit time,

J/sec or kcal/hr

$\overline{s}$ = specific entropy, J/kmol·K or kcal/kmol·K

$\overline{s}_0$ = specific entropy at the dead state, J/kmol·K or kcal/kmol·K

T = temperature of system A, K

T_{m1} = temperature of system M1, K

T_{m2} = temperature of system M2, K

T_0 = temperature at the dead state, K

$|(W_x)_0|$ = work loss to the environment except that due to the expansion

of the boundaries of system A per unit time, J/sec or kcal/hr

$|W_1|$ = work supplied from the work source, system N1, to system A per unit time, J/sec or kcal/hr

$|W_2|$ = work supplied from system A to the work source, system N2 per unit time, J/sec or kcal/hr

GREEK

$\bar{\beta}$ = partial molar enthalpy relative to the dead state, J/kmol or kcal/kmol

$\bar{\beta}^0$ = specific chemical enthalpy, J/kmol or kcal/kmol

$\bar{\gamma}$ = partial molar entropy relative to the dead state, J/kmol·K

$\bar{\gamma}^0$ = specific chemical entropy, J/kmol·K or kcal/kmol·K

$\bar{\epsilon}$ = partial molar exergy, J/kmol or kcal/kmol

$\bar{\epsilon}^0$ = specific chemical exergy, J/kmol or kcal/kmol

η_m = mass utilization efficiency

$(\eta_1)_D$ = thermodynamic first-law incremental efficiency

$(\eta_1)_P$ = thermodynamic first-law process efficiency

$(\eta_2)_D$ = thermodynamic second-law incremental efficiency

$(\eta_2)_P$ = thermodynamic second-law process efficiency

σ = created entropy per unit time, J/K·sec or kcal/K·hr

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Table 1. Compositions, β^0 and ε^0 of refuse and char.

	Refuse (wt%**)	Char (wt%**)
C	26.0	24.29
H	3.5	0.57
O	20.5	3.71
Moisture	25.0	—
Ash	25.0	71.43
Total	100	100
	Refuse	Char
β^{0*}, kcal/kg	2,583	1,951
ε^{0*}, kcal/kg	2,686	1,038

* $\beta^0 \equiv h^0 - h_0$,

$\varepsilon^0 \equiv (h^0 - h_0) - T_0(s^0 - s_0)$.

** Total weight or wet basis.

Table 2. Components, their concentrations, β^0 and ε^0 of product and flue gases.

	Product Gas (wt%**)	Flue Gas (wt%**)
CO_2 (g)	10.4	12.5
CO (g)	2.7	——
CH_4 (g)	1.5	——
H_2 (g)	0.9	——
C_2H_4 (g)	0.7	——
N_2 (g)	38.3	60.5
H_2O (g)	42.9	25.2
Organic (g)	2.6	——
O_2 (g)	——	1.8
Total	100	100

	Product Gas	Flue Gas
β^{0*}, kcal/kg	1,109	147.2
ε^{0*}, kcal/kg	847.9	45.93

* $\beta^0 \equiv h^0 - h_0$,

$\varepsilon^0 \equiv (h^0 - h_0) - T_0(s^0 - s_0).$

** Total weight basis.

Table 3. Flow conditions, enthalpy content and exergy content of each stream, and work requirement.

	Flow Rate (kg/hr)	T (K)	P (atm)	β (kcal/kg)	ε (kcal/kg)	Π_{av} (10^3kcal/hr)	A_{ex} (10^3kcal/hr)
1. Air	731	298.15	1	0	0	0	0
2. Refuse	1,000	298.15	1	2,583	2,686	2,686	2,583
3. Char	350	1,033.15	1	2,105	2,115	736.8	740.2
4. Product. Gas	1,381	1,033.15	1	1,263	924.4	1,745	1,227
5. Water	1,772	298.15	1	0	0	0	0
6. Water	1,772	298.15	25	0.5827	0.5827	1.033	1.033
7. Air	1,719	298.15	1	0	0	0	0
8. Flue Gas	3,100	533.15	1	175.4	53.34	543.8	165.3
9. Steam	1,772	533.15	20	674.8	230.9	1,196	409.1
$|W_p|$	—	—	—	—	—	1.45	1.45

Note: $\beta = h - h_0$, $\varepsilon = (h - h_0) - T_0(s - s_0)$

Table 4. Energy consumption, $(H_{av})_c$, energy dissipation, $(A_{ex})_{dis}$, and
efficiencies of each subsystem and the overall system for each
operating mode.

	Pyrolizer	Pump	Burner and Boiler	Overall System
$(H_{av})_c$ $(10^3$ kcal/hr)	101.65	0.4174	6.0026	108.07
% [a]	94.06	0.39	5.55	100
$(A_{ex})_{dis}$ $(10^3$ kcal/hr)	668.78	0.4174	703.16	1372.4
% [b]	48.73	0.03	51.24	100
$(\eta_1)_{P1}$, %	67.54	71.12	68.50	46.27
$(\eta_1)_{P2}$, %	67.54	71.12	99.66	67.31
$(\eta_1)_{P3}$, %	96.06	71.12	68.50	74.78
$(\eta_1)_{P4}$, %	96.06	71.12	99.66	95.82
$(\eta_2)_{P1}$, %	50.22	71.12	32.02	15.23
$(\eta_2)_{P2}$, %	50.22	71.12	44.96	21.38
$(\eta_2)_{P3}$, %	77.79	71.12	32.02	42.77
$(\eta_2)_{P4}$, %	77.79	71.12	44.96	48.93
$(\eta_1)_D$, %	--	71.12	99.50	91.71
$(\eta_2)_D$, %	--	71.12	36.72	22.97

a) Percentage contribution to the total energy consumption.
b) Percentage contribution to the total available energy dissipation.
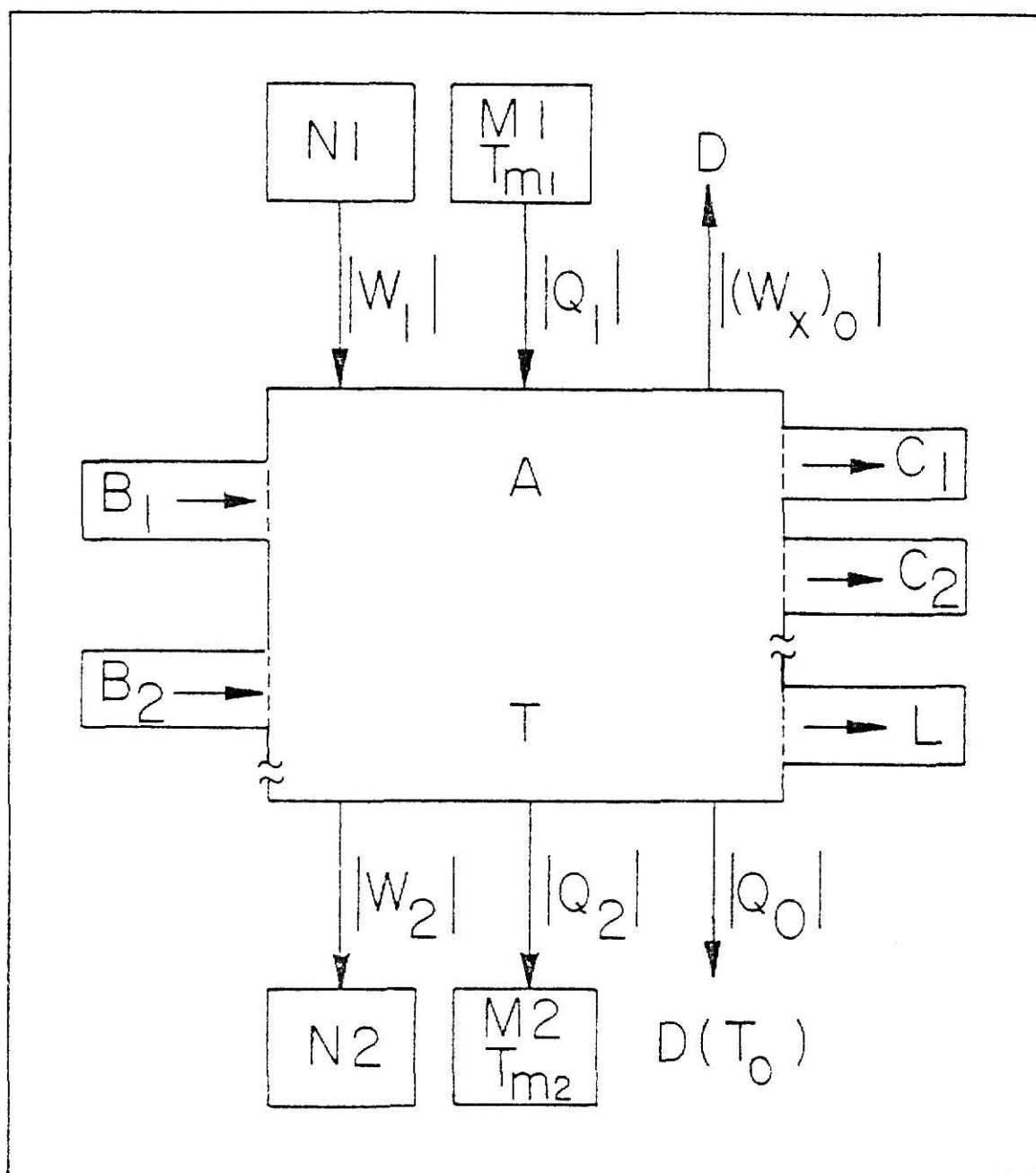
Fig. I. Schematic diagram of an open flow system.
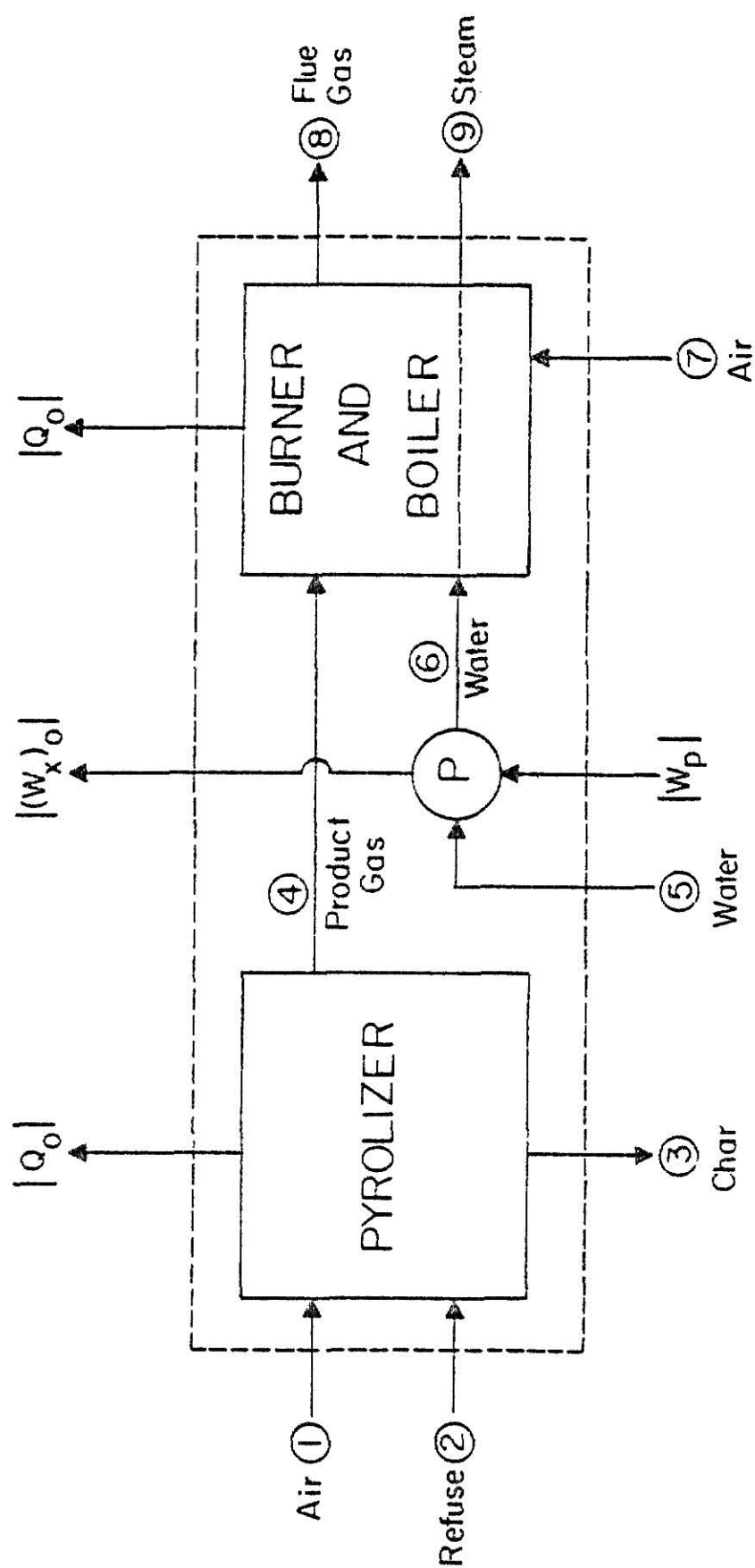
Fig. 2. Biomass pyrolysis system.
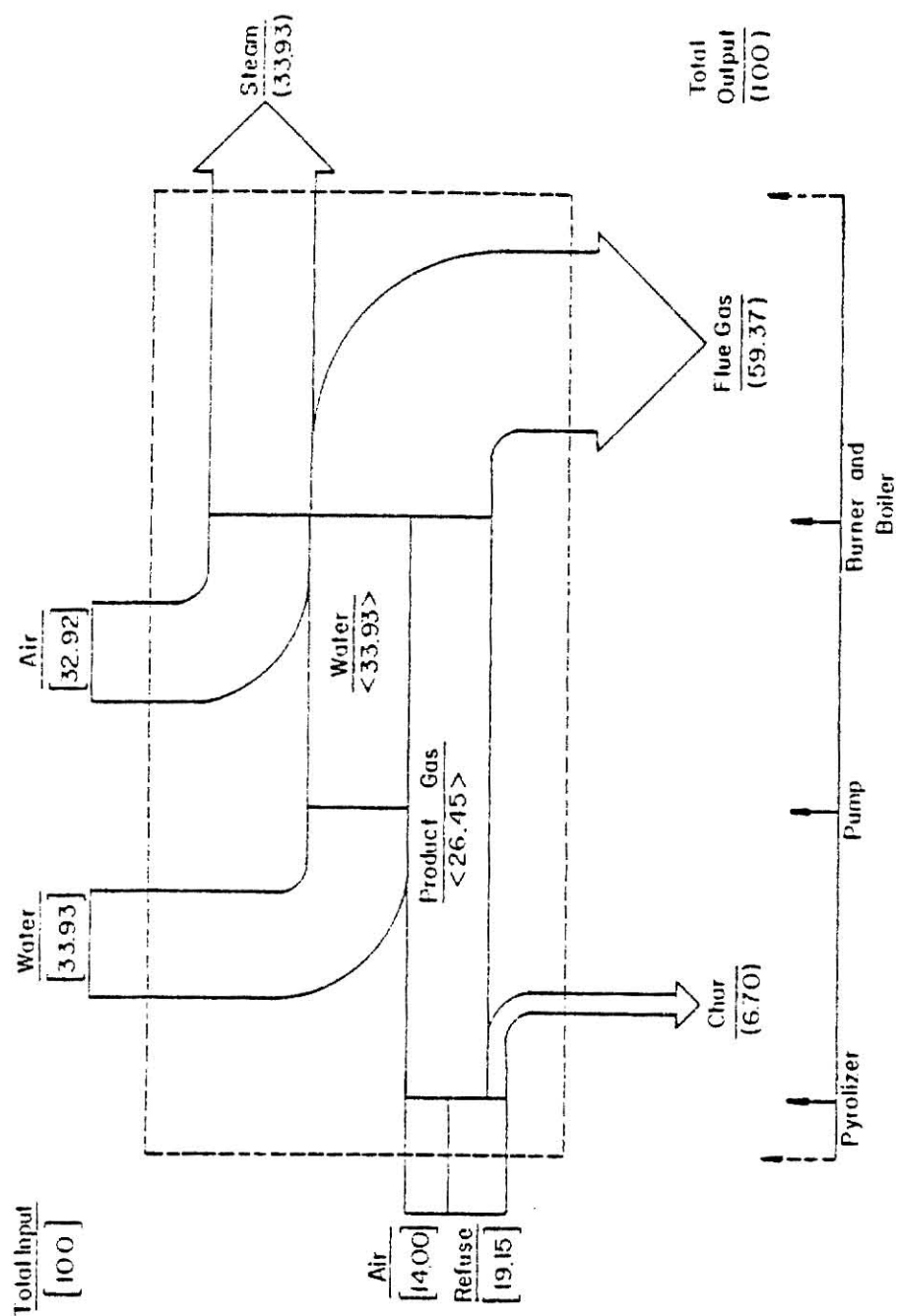
Fig. 3. Mass flow diagram for the biomass pyrolysis process : operating mode P4.
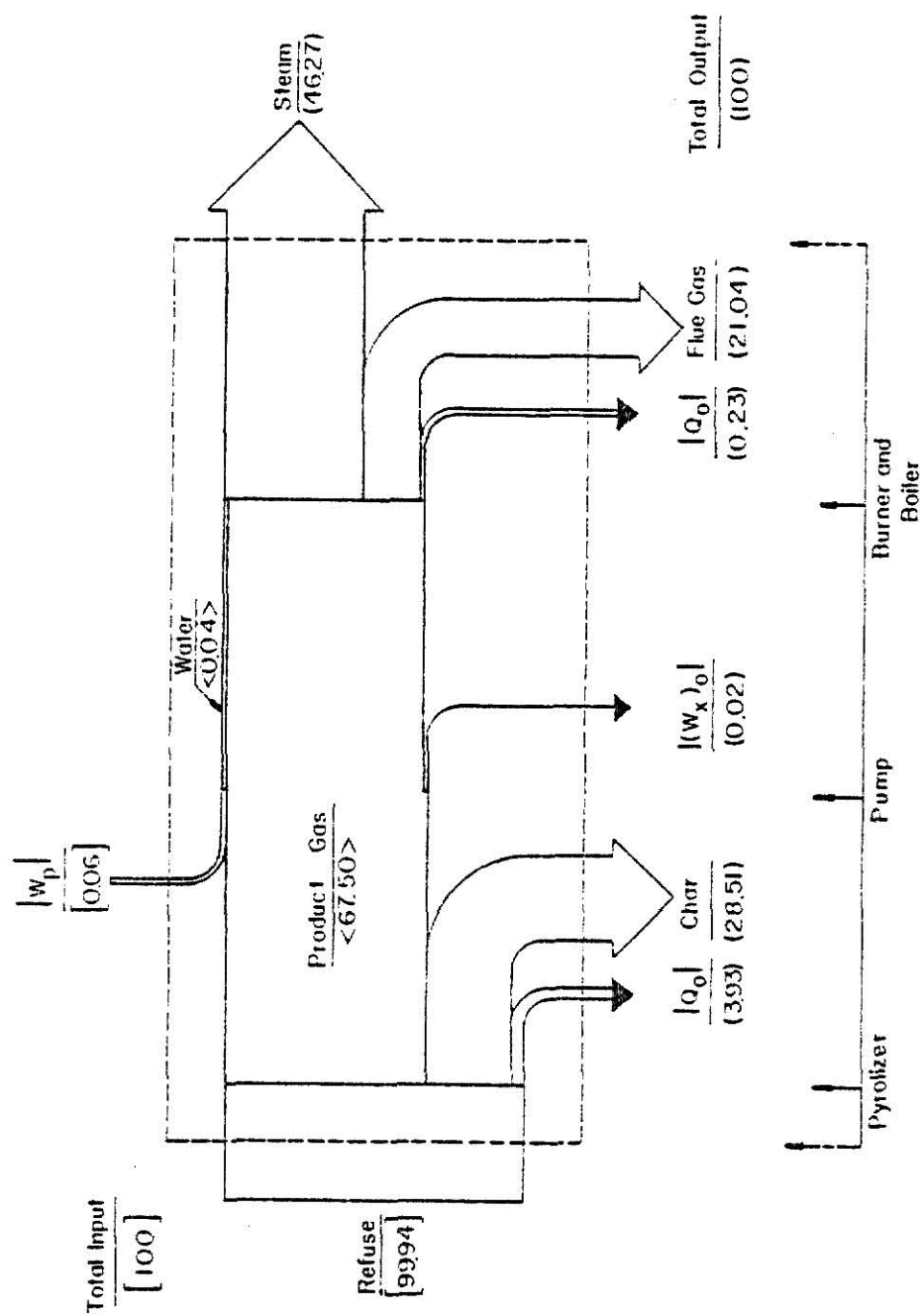
Fig.4. Energy flow diagram for the biomass pyrolysis process : operating mode P4.
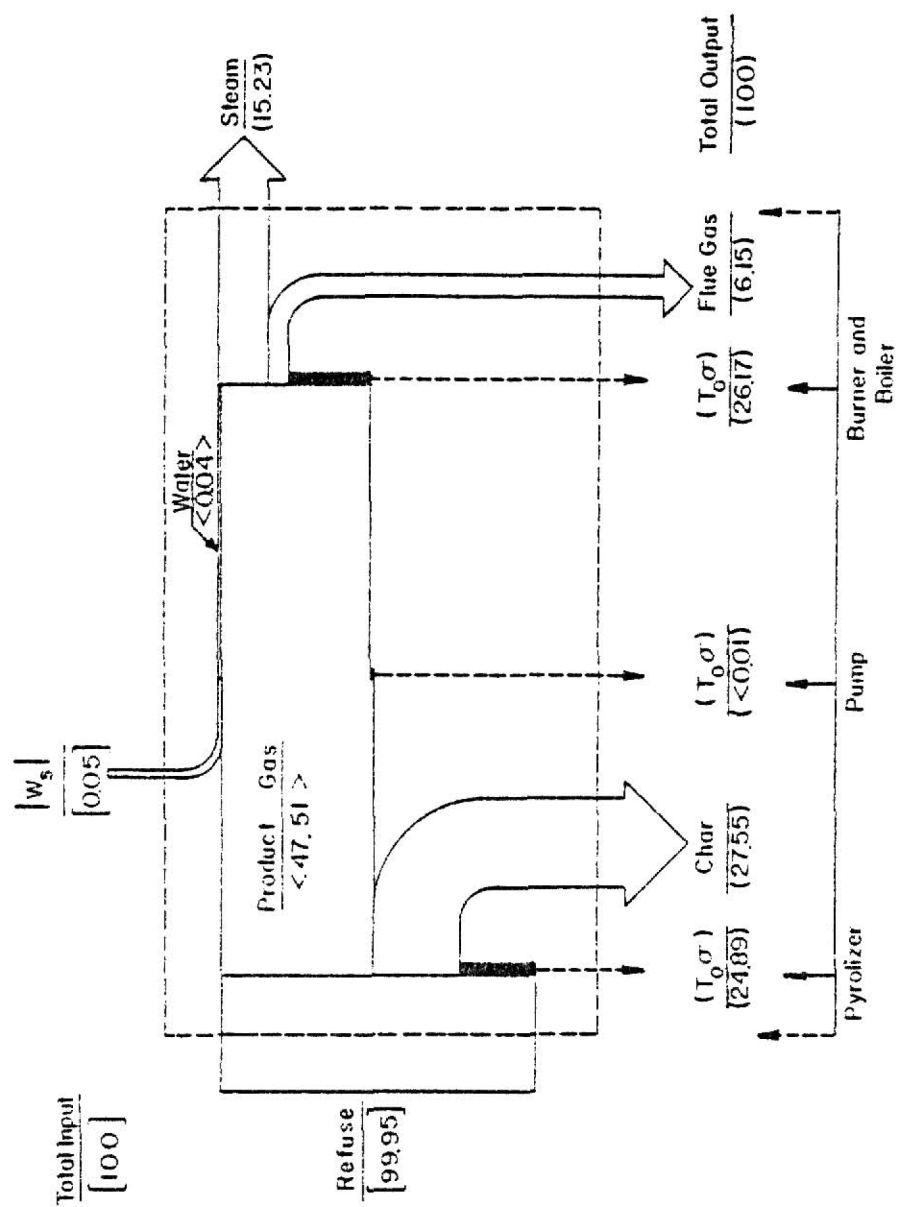
Fig. 5. Available energy flow diagram for the biomass pyrolysis process : operating mode P 4.

CHAPTER 6

THERMODYNAMIC ANALYSIS OF

AN ANAEROBIC DIGESTION PROCESS

THERMODYNAMIC ANALYSIS OF
AN ANAEROBIC DIGESTION PROCESS

Anaerobic digestion in wastewater treatment has the function of
stabilizing organic sludges and reducing the sludge volume for ultimate
disposal (see, e.g., USEPA, 1979; Grady and Lim, 1980). The gas produced
in this step of wastewater treatment contains mainly CH_4, CO_2 and H_2O;
the gas produced has been exploited for various end uses ever since the
discovery of its combustibility. Several means are available for utilizing
this by-product of anaerobic digestion. It can be used directly by means
of combustion for lighting, heating and cooking. It can be also conver-
ted into mechanical shaft work or electricity (see, e.g., Iwai et al., 1974;
Pacific Northwest Laboratory, 1981; Owen, 1982). User requirements, economy,
social demand and environmental concern would govern the mode of utili-
zation of the digester gas.

In this chapter, thermodynamic analysis and preliminary optimization
studies have been carried out for the anaerobic digestion process. The
procedure employed determines the efficiencies of the system from the
viewpoint of the thermodynamic first and second laws; it also enables
us to identify the nature and location of the thermodynamic inefficiency.
The effects of structural modification of the process through incorporation
of a gas engine and variation in the operating scheme have been examined.
For covenience, some of the governing equations for this system analysis,
derived in Chapter 3, are repeated in the succeeding section.

PROCEDURE

The procedure employed in this work is based on the law of mass conservation and on the first and second laws of thermodynamics, which lead to the mass, energy and entropy balances of a process system. The combination of the energy and entropy balances gives rise to the available energy balance which, in turn, yields the concept of essergy under unsteady-state conditions and that of exergy under steady-state conditions (see, e.g., Keenan, 1941, 1951; Rant, 1956; Evans, 1969; Gaggioli, 1980; Fan and Shieh, 1980).

In this section, the expressions of the mass, energy, entropy and available energy balances of an unsteady-state open flow system are presented, and then they are reduced to the corresponding balances of a steady-state open flow system. The definition of the mass utilization efficiency and those of the thermodynamic first-law and second-law efficiencies of the steady-state open flow system are also given (see, e.g., Denbigh, 1956, 1971; Szargut and Petela, 1965; Riekert, 1974; Gaggioli and Petit, 1977; Fan et. al., 1982). Figure 1 illustrates an overall process system identified for the purpose of writing explicitly such balances. It includes system A (an unsteady-state open flow system with multiple input and output streams), system M1 (a heat source at temperature T_{m1}), system M2 (a heat sink at temperature T_{m2}), system N1 (a work source), system N2 (a work sink), and the surroundings, D.

Mass Balance

Applying the law of mass conservation to system A, transforming from state 1 at t = 0 to state 2 at t = t, yields

$$\{M_{A2}(t) - M_{A1}\}$$

$$= \sum_i \{\int_0^t \sum_k [(Mw)_k n_k(t)]\, dt\}_i$$

$$- \sum_e \{\int_0^t \sum_k [(Mw)_k n_k(t)]\, dt\}_e$$

$$- \sum_\ell \{\int_0^t \sum_k [(Mw)_k n_k(t)]\, dt\}_\ell \qquad (1)$$

where n is the molar flow rate including both the convective and diffusional

flows. For a steady-state system, this equation becomes

$$\sum_i [\sum_k (Mw)_k n_k]_i = \sum_e [\sum_k (Mw)_k n_k]_e + \sum_\ell [\sum_k (Mw)_k n_k]_\ell \qquad (2)$$

or

$$\sum M_i = \sum M_{e,u} + \sum M_{e,d} + \sum M_\ell \qquad (3)$$

where i stands for the input streams, e for the output streams, u for the

recovered or usable streams, d for the wasted or discarded streams and ℓ

for the leakage streams.

Energy Balance

Applying the first law of thermodynamics to system A, the energy bal-

ance can be expressed as

$$[E_{A2}(t) - E_{A1}] - [(E_0)_{A2}(t) - (E_0)_{A1}]$$

$$+ P_0[V_{A2}(t) - V_{A1}] - P_0[(V_0)_{A2}(t) - (V_0)_{A1}]$$

$$= \sum_i \{\int_0^t \sum_k [(\overline{\beta}(t) + X_g(t) + \frac{U(t)^2}{2} + \ldots)_k \ n_k(t)]dt\}_i$$

$$- \sum_e \{\int_0^t \sum_k [(\overline{\beta}(t) + X_g(t) + \frac{U(t)^2}{2} + \ldots)_k \ n_k(t)]dt\}_e$$

$$- \sum_\ell \{\int_0^t \sum_k [(\overline{\beta}(t) + X_g(t) + \frac{U(t)^2}{2} + \ldots)_k \ n_k(t)]dt\}_\ell$$

$$+ \int_0^t [|Q_1(t)| - |Q_2(t)| - |Q_0(t)|]dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)| - |(W_x)_0(t)|]dt \tag{4}$$

where $\overline{\beta}$ is the partial molar enthalpy relative to the dead state defined as

$$\overline{\beta} \equiv \overline{h} - \overline{h}_0 \tag{5}$$

and subscript 0 stands for the dead state. Provided that the potential energy, kinetic energy, etc. are negligible, for a steady-state system, equation (4) reduces to

$$[\sum_i (\sum_k \overline{\beta}_k n_k)_i + |Q_1| + |W_1|]$$

$$= [\sum_e (\sum_k \overline{\beta}_k n_k)_e + |Q_2| + |W_2|] + [\sum_\ell (\sum_k \overline{\beta}_k n_k)_\ell]$$

$$+ [|Q_0| + |(W_x)_0|] \tag{6}$$

When one or more of the exit streams are discarded because they contain useless by-products or wastes, the first term of the right hand side of this equation, $[\Sigma(\Sigma\overline{\beta}_k n_k)_e + |Q_2| + |W_2|]$, can be divided into the recovered or usable part indicated by subscript u and the wasted or discarded part indicated by subscript d. Therefore, equation (6) can be rewritten as

$$[\Sigma(H_{av})_i] = [\Sigma(H_{av})_{e,u} + \Sigma(H_{av})_{e,d}] + [\Sigma(H_{av})_\ell] + [\Sigma(H_{av})_c] \quad (7)$$

where subscript ℓ indicates the leakage and subscript c the consumption. Obviously, $[\Sigma(H_{av})_i]$ corresponds to the left hand side, and $[\Sigma(H_{av})_{e,u} + \Sigma(H_{av})_{e,d}]$, $[\Sigma(H_{av})_\ell]$, and $[\Sigma(H_{av})_c]$ correspond, respectively, to the first, second, and third terms of the right hand side of equation (6), all bracketed by [ ].

Suppose that i_1 (or i_2) number of the inlet streams can be identified as the streams which lose (or gain) enthalpy contents to become e_1 (or e_2) number of the exit streams and ℓ_1 (or ℓ_2) number of the leakage streams, during their passage through system A. Then, equation (6) can be expressed in the so-called incremental form as

$$\{[\sum_{i_1}\sum_k (\Sigma\overline{\beta}_k n_k)_{i_1} - \sum_{e_1}\sum_k (\Sigma\overline{\beta}_k n_k)_{e_1} - \sum_{\ell_1}\sum_k (\Sigma\overline{\beta}_k n_k)_{\ell_1}] + [|Q_1| + |W_1|]\}$$

$$= \{[\sum_{e_2}\sum_k (\Sigma\overline{\beta}_k n_k)_{e_2} + \sum_{\ell_2}\sum_k (\Sigma\overline{\beta}_k n_k)_{\ell_2} - \sum_{i_2}\sum_k (\Sigma\overline{\beta}_k n_k)_{i_2}] + [|Q_2| + |W_2|]\}$$

$$+ \{|Q_0| + |(W_x)_0|\} \quad (8)$$

This equation can be rewritten as

$$\{\Sigma(H_{av})_i\}_D = \{\Sigma(H_{av})_e\}_D + \{\Sigma(H_{av})_c\} \quad (9)$$

where $\{\Sigma(H_{av})_i\}_D$ is the energy transferred to system A from energy sources, including heat sources, work sources and process streams which lose energy contents during their passage through the system, $\{\Sigma(H_{av})_i\}_D$ is energy transferred by system A to energy sinks, including heat sinks, work sinks and process streams which gain energy contents during their passage through the system, and $\{\Sigma(H_{av})_c\}$ is the energy consumption due to the loss through the walls of system A. In other words, there exists a one-to-one correspondence between the equivalent terms in equations (8) and (9), all grouped by brackets, { }.

Entropy Balance

The statement of the second law of thermodynamics for the entire system, including not only system A but also all other subsystems and the surroundings shown in Fig. 1, can be expressed as

$$
\int_0^t \sigma(t)dt = [S_{A2}(t) - S_{A1}] - [(S_0)_{A2}(t) - (S_0)_{A1}]
$$

$$
- \{ \Sigma \int_0^t \Sigma [\overline{\gamma}_k(t) \; n_k(t)]dt \}_i
$$

$$
+ \Sigma \{ \int_0^t \Sigma [\overline{\gamma}_k(t) \; n_k(t)]dt \}_e
$$

$$
+ \Sigma \{ \int_0^t \Sigma [\overline{\gamma}_k(t) \; n_k(t)]dt \}_\ell
$$

$$
+ \int_0^t [-\frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0}]dt \qquad (10)
$$

where σ denotes the created entropy or entropy generation, and $\overline{\gamma}$ is the partial molar entropy relative to the dead state defined as

$$\bar{\gamma} \equiv \bar{s} - \bar{s}_0 \tag{11}$$

For a steady state process, equation (10) reduces to

$$\sum_i (\sum_k \bar{\gamma}_k n_k)_i + \frac{|Q_1|}{T_{m1}}$$

$$= \sum_e (\sum_k \bar{\gamma}_k n_k)_e + \sum_\ell (\sum_k \bar{\gamma}_k n_k)_\ell + \frac{|Q_2|}{T_{m2}} + \frac{|Q_0|}{T_0} - \sigma \tag{12}$$

Available Energy Balance

Combination of equation (4), the energy balance, and equation (10), the entropy balance, gives rise to

$$\{[E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)]$$

$$- [(E_0)_{A2}(t) + P_0(V_0)_{A2}(t) - T_0(S_0)_{A2}(t)]\}$$

$$- \{[E_{A1} + P_0 V_{A1} - T_0 S_{A1}] - [(E_0)_{A1} + P_0(V_0)_{A1} - T_0(S_0)_{A1}]\}$$

$$= \sum_i \{\int_0^t \sum_k [(\bar{\varepsilon}(t) + X_g(t) + \frac{U(t)^2}{2} + \ldots)_k \ n_k(t)]dt\}_i$$

$$- \sum_e \{\int_0^t \sum_k [(\bar{\varepsilon}(t) + X_g(t) + \frac{U(t)^2}{2} + \ldots)_k \ n_k(t)]dt\}_e$$

$$- \sum_\ell \{\int_0^t \sum_k [(\bar{\varepsilon}(t) + X_g(t) + \frac{U(t)^2}{2} + \ldots)_k \ n_k(t)]dt\}_\ell$$

$$+ \int_0^t [|Q_1(t)| \ (1 - \frac{T_0}{T_{m1}}) - |Q_2(t)| \ (1 - \frac{T_0}{T_{m2}}) + |W_1(t)| - W_2(t)|]dt$$

$$- \int_0^t [|(W_x)_0(t)| + (T_0 \sigma(t))]dt \tag{13}$$

where $\bar{\varepsilon}$ is the partial molar exergy defined as

$$\bar{\varepsilon} \equiv (\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0)$$

$$= \bar{\beta} - T_0 \bar{\gamma} \tag{14}$$

For a steady-state system having negligible kinetic energy, potential energy, etc., equation (13) reduces to

$$[\sum_i (\sum_k \overline{\varepsilon}_k n_k)_i + |Q_1| \, (1 - \frac{T_0}{T_{m1}}) + |W_1|]$$

$$= [\sum_e (\sum_k \overline{\varepsilon}_k n_k)_e + |Q_2| \, (1 - \frac{T_0}{T_{m2}}) + |W_2|] + [\sum_\ell (\sum_k \overline{\varepsilon}_k n_k)_\ell]$$

$$+ [|(W_x)_0| + (T_0 \sigma)] \tag{15}$$

Similar to equation (7), equation (15) can be compactly expressed as

$$[\sum (A_{ex})_i] = [\sum (A_{ex})_{e,u} + \sum (A_{ex})_{e,d}] + [\sum (A_{ex})_\ell] + [\sum (A_{ex})_{dis}] \tag{16}$$

where subscript dis stands for the available energy dissipation due to all kinds of irreversibility. Obviously, $[\sum (A_{ex})_i]$ corresponds to the left hand side of equation (15), and $[\sum (A_{ex})_{e,u} + \sum (A_{ex})_{e,d}]$, $[\sum (A_{ex})_\ell]$ and $[\sum (A_{ex})_{dis}]$ correspond, respectively, to the first, second and third terms of the right hand side of equation (15), all bracketed by [ ]. Again similar to equations (8) and (9), equation (15) can be rewritten as

$$\{ [\sum_{i_1} (\sum_k \overline{\varepsilon}_k n_k)_{i_1} - \sum_{e_1} (\sum_k \overline{\varepsilon}_k n_k)_{e_1} - \sum_{\ell_1} (\sum_k \overline{\varepsilon}_k n_k)_{\ell_1}]$$

$$+ [|Q_1| \, (1 - \frac{T_0}{T_{m1}}) + |W_1|] \}$$

$$= \{ [\sum_{e_2} (\sum_k \overline{\varepsilon}_k n_k)_{e_2} + \sum_{\ell_2} (\sum_k \overline{\varepsilon}_k n_k)_{\ell_2} - \sum_{i_2} (\sum_k \overline{\varepsilon}_k n_k)_{i_2}]$$

$$+ \left[|Q_2| \left(1 - \frac{T_0}{T_{m2}}\right) + |W_2| \right] \}$$

$$+ \{ |(W_x)_0| + (T_0 \sigma) \} \tag{17}$$

and

$$\{ \Sigma (A_{ex})_i \}_D = \{ \Sigma (A_{ex})_e \}_D + \{ \Sigma (A_{ex})_{dis} \} \tag{18}$$

where $\{ \Sigma (A_{ex})_i \}_D$ is the available energy transferred to system A from the energy sources, including heat sources, work sources and process streams which lose available energy contents during their passage through the system, $\{ \Sigma (A_{ex})_e \}_D$ is the available energy transferred from system A to energy sinks, including heat sinks, work sinks and process streams which gain available energy contents during their passage through the system, and $\Sigma (A_{ex})_{dis}$ is the available energy dissipation. In other words, there exists a one-to-one correspondence between the equivalent terms in equations (17) and (18), all grouped by brackets, { }.

Thermodynamic Efficiencies

The mass utilization efficiency and the thermodynamic first-law and second-law efficiencies can be defined meaningfully on the basis of the mass, energy and available energy balances, respectively. From equation (3), the mass utilization efficiency can be expressed as

$$\eta_m = \frac{\Sigma M_{e,u}}{\Sigma M_i} \tag{19}$$

The first-law process and incremental (or extractive) efficiencies of a process system can be expressed from equations (7) and (9), respectively, as

$$(\eta_1)_P = \frac{[\Sigma (H_{av})_{e,u}]}{[\Sigma (H_{av})_i]} \tag{20}$$

$$(\eta_1)_D \;=\; \frac{\{\Sigma(H_{av})_e\}_D}{\{\Sigma(H_{av})_i\}_D} \tag{21}$$

Similarly, the second-law process and incremental efficiencies can be expressed from equations (16) and (18), respectively, as

$$(\eta_2)_P \;=\; \frac{[\Sigma(A_{ex})_{e,u}]}{[\Sigma(A_{ex})_i \;]} \tag{22}$$

$$(\eta_2)_D \;=\; \frac{\{\Sigma(A_{ex})_e\}_D}{\{\Sigma(A_{ex})_i\}_D} \tag{23}$$

Computational Steps

Equations (3), (7), (9), (16) and (18) indicate that, broadly speaking, the causes of thermal inefficiency are: (a) energy loss from the walls of the system to the surroundings, $[\Sigma(H_{av})_c]$, (b) available energy dissipation due to all types of irreversibilities, $[\Sigma(A_{ex})_{dis}]$, (c) combined effect of the energy loss associated with the discarded material streams and the material leakage, and that from the walls of the system to the surroundings, $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_\ell + \Sigma(H_{av})_c]$, and (d) combined effect of the available energy loss associated with the discarded material streams and the material leakage, and the available energy dissipation due to all types of irreversibilities, $[\Sigma(A_{ex})_{e,d} + \Sigma(A_{ex})_\ell + \Sigma(A_{ex})_{dis}]$.

Explicit inclusion of the expression for the mass balance, equation (3), and that for the mass utilization efficiency, equation (19), in the present approach has been prompted by the fact that the material wastage and leakage can affect drastically and negatively the thermodynamic efficiencies of a process system as indicated by equations (20) through (23). Furthermore, $[\Sigma(H_{av})_c]$ is imbedded in $[\Sigma(A_{ex})_{dis}]$ and $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_\ell + \Sigma(H_{av})_c]$, and these quantities, in turn, are imbedded in $[\Sigma(A_{ex})_{e,d} + \Sigma(A_{ex})_\ell + \Sigma(A_{ex})_{dis}]$. Thus, the principle of optimality (Bellman, 1957) indicates that a logical sequence exists for thermodynamically analyzing a process system to identify the nature and sources of thermodynamic inefficiencies. The sequence is as follows:

Step 1. Evaluation of the material wastage, $\Sigma M_{e,d}$, and the material leakage, ΣM_ℓ, by equation (3) and the mass utilization efficiency, η_m, by equation (19).

Step 2.   Evaluation of the energy consumption, $[\Sigma(H_{av})_c]$, and

the first-law incremental efficiency, $(\eta_1)_D$, by

equations (9) and (21), respectively.

Step 3.   Evaluation of the available energy dissipation,

$[\Sigma(A_{ex})_{dis}]$, and the second-law incremental efficiency,

$(\eta_2)_D$, by equations (18) and (23), respectively.

Step 4.   Evaluation of the energy loss, $[\Sigma(H_{av})_{e,d} + \Sigma(H_{av})_\ell$

$+ \Sigma(H_{av})_c]$, and the first-law process efficiency,

$(\eta_1)_p$, by equations (7) and (20), respectively.

Step 5.   Evaluation of the available energy loss, $[\Sigma(A_{ex})_{e,d}$

$+ \Sigma(A_{ex})_\ell + \Sigma(A_{ex})_{dis}]$, and the second-law process

efficiency, $(\eta_2)_p$, by equations (16) and (22), re-

spectively.

The results will indicate the possible remedial measures for reducing or

eliminating the sources of thermodynamic inefficiencies identified.

PROCESS DESCRIPTION

The process under consideration is an anaerobic sludge digestion process in which organic sludges are stabilized and anaerobically converted mainly into methane (CH_4) and carbon dioxide (CO_2) (see, e.g., Iwai et al., 1974; USEPA, 1979; Grady and Lim, 1980). The influent to the digester tank is a mixture of primary sludge and activated sludge, and its rate of flow is 120,000 kg/day (264,000 lb/day) with a total solid percentage of 3.0% as shown in Table 1. This table also shows that the solid contents in the influent consist of 36.50% carbon, 5.35% hydrogen, 4.35% nitrogen, 25.00% oxygen and 28.80% ash by weight. The anaerobic digestion process is a conventional one, consuming 50% volatile solids to produce digester gas at a rate of 1,459 kg/day (3,200 lb/day). The effluent rate from the digester tank is 118,540 kg/day (261,000 lb/day) with a total solid percentage of 2.0% as shown in Table 1. The elemental analysis of the effluent is also shown in the table. To attain an optimal digestion rate, the sludge in the digester tank is mixed mechanically and heated by hot water to maintain a temperature of 308.15 K (95°F).

The generated digester gas is taken as a useful by-product for off-site usage in the basic process of the system consisting only of a digester, as shown in Fig. 2. While the digester gas can be consumed directly for a variety of purposes, we are often faced with the need of converting at least part of its energy content into different forms, i.e., electrical or shaft power (see, e.g., Ward, 1974; Pacific Northwest Laboratory, 1981; Owen, 1982). Thus, the basic process is modified according to the procedure described in the succeeding part. The modified process is generated by coupling a gas engine and a heat exchanger with the basic process

(Fig. 3). The digester gas is sent to the gas engine to be converted into the mechanical and/or electrical energy which may be used to power pumps and blowers. The rest of the digester gas is supplied for off-site usage. Hot water from the cooling jacket is pumped to the heat exchanger where it is heated further by the flue gas from the engine; the hot water is utilized to maintain the temperature of the digester tank. The flue gas from the heat exchanger is discarded to the surroundings at 473.15 K (392°F). Several operating schemes of the modified process are considered. They are as follows:

Scheme 1. Less than 48.78% of the digester gas produced is allocated to the gas engine. Since the hot water from the gas engine subsystem is insufficient for heating the sludge, it is supplemented from an outside source.

Scheme 2. 48.78% of the digester gas produced is allocated to the gas engine. Energy requirement for heating the sludge and energy supplied by the hot water are exactly balanced.

Scheme 3. More than 48.78% of the digester gas produced is allocated to the gas engine. The hot water recovered from the gas engine subsystem exceeds the requirement for heating the sludge. Two variants of this operating scheme are considered, namely, scheme 3-P1 where excess hot water is discarded to the surroundings, and scheme 3-P2 where excess hot water is recovered for usage outside the system.

Scheme 4. 100% of the digester gas produced is allocated to the gas engine. Similar to scheme 3, two variants,

scheme 4-P1, corresponding to scheme 3-P1, and

scheme 4-P2, corresponding to scheme 3-P2, are

considered.

Obviously, both structural modification of the process and variation in the

operating scheme will affect the thermodynamic efficiency of the system.

RESULTS AND DISCUSSION

The results are summarized in Tables 1 through 10, and illustrated in Figs. 1 through 8. Table 1 lists the flow rates and compositions for the influent and effluent of the digester tank. The compositions of the digester gas produced and the flue gas exhausted from the gas engine are tabulated in Table 2. The flow rate, temperature, pressure, energy content and available energy content of each stream for the basic process shown in Fig. 2, and the operating schemes, 1, 2, 3 and 4, of the modified process shown in Fig. 3, are summarized in Tables 3, 4, 5, 6 and 7, respectively; Table 8 lists the work requirements and generations, and Table 9 gives the energy consumptions, the available energy dissipations, and the efficiencies for these processes. In operating schemes 2 and 4, the fractions of the digester gas allocated to the gas engine, x, are fixed as mentioned in the previous section; they are 0.4878 (or 48.78%) and 1 (or 100%), respectively. For operating schemes 1 and 3, they are constrained in specific ranges; they are $0 < x < 0.4878$ for operating scheme 1 and $0.4878 < x < 1$ for operating scheme 3. For simplicity and convenience in comparison, however, Tables 4, 6, 8, 9 and 10 contain only the results for $x = 0.25$ (or 25%) and $x = 0.75$ (or 75%) for schemes 1 and 3, respectively.

Digester Gas Production

Tables 1 through 3 reveal that the anaerobic sludge digester itself processes the sludge at a rate of 120,000 kg/day, which has the energy content of 112.5 kcal/kg and the available energy content of 114.2 kcal/kg, and yields digester gas with relatively high energy and available energy contents of 5,196 kcal/kg and 4,891 kcal/kg, respectively, at a rate of 1,459 kg/day.

These tables also reveal that almost half of the elementary carbon, hydrogen and oxygen in the feed sludge is converted into the gaseous product from the digester, containing 38.89% methane, 57.58% carbon dioxide and 3.53% water vapor by weight, and the elementary nitrogen remains uncoverted. The sludge is withdrawn from the digester at a rate of 118,540 kg/day, which has energy and available energy contents of 60.55 kcal/kg and 52.39 kcal/kg, respectively. Therfore, during the passage through the digester, the reductions in energy and available energy contents of the sludge are around 46% and 54%, respectively. The generated gas can be directly consumed as fuel, as in the case of the basic process, or can be conveyed to the gas engine for conversion into the shaft work or electricity as in the case of the modified process as stated earlier.

Work Generation

It is assumed that the efficiency of the gas engine employed in the modified process is such that it converts 30% of the energy or 32% of the available energy in the digester gas supplied to it. Part of the work generated in the gas engine is used for pumping the process streams and for mixing the sludge in the digester tank as indicated in Fig. 3 and Table 8; consequently, the net amounts of work generated from the modified process are 517.4×10^3 kcal/day (601.6 kwh/day), $1,056 \times 10^3$ kcal/day (1,228 kwh/day), $1,650 \times 10^3$ kcal/day (1,919 kwh/day) and $2,218 \times 10^3$ kcal/day (2,579 kwh/day) for the operating schemes, 1, 2, 3 and 4, respectively. The hot water from the gas engine subsystem is utilized to heat sludge; besides, it is useful for outside usage, e.g., heating buildings.

Approximately 40% of the energy content of the digester gas is recovered in the gas engine subsystem by cooling water; however, the extent

of recovery of the available energy content is only around 6%. Obviously, the difference between them is substantial. For the operating schemes, 3-P2 and 4-P2, the rates of heated cooling water recovered from the gas engine subsystem for the outside usage are 11,640 kg/day and 22,730 kg/day, respectively, at 368.15 K, which has the energy content of 70.05 kcal/kg and the low available energy content of 7.170 kcal/kg. The flue gas exhausted from the gas engine subsystem has the energy and available energy contents of 104.8 kcal/kg and 45.01 kcal/kg, respectively, in all schemes.

Energy Consumption, Available Energy Dissipation and Efficiencies

Table 9 lists the energy consumption, available energy dissipation and efficiencies for the basic process and each operating scheme of the modified process. The energy consumptions in the overall systems are as follows: 171.6×10^3 for the basic process, and 375.6×10^3, 568.5×10^3, 782.9×10^3 and 986.6×10^3 kcal/day for the operating schemes, 1, 2, 3 and 4, of the modified process, respectively. The available energy dissipations in the overall systems are as follows: 610.2×10^3 for the basic process, and $1,569 \times 10^3$, $2,477 \times 10^3$, $3,519 \times 10^3$ and $4,507 \times 10^3$ kcal/day for the operating schemes, 1, 2, 3 and 4, of the modified process, respectively. The energy consumption and available energy dissipation in the digester subsystem for each operating scheme are constant, while those of the gas engine subsystem are increased considerably as the fraction of the digester gas allocated to the gas engine, x, increases. The thermodynamic first-law process efficiencies of the overall systems are 46.48%, 41.63%, 36.45%, 26.16% and 16.37%, and the thermodynamic second-law process efficiencies are 50.86%, 42.25%, 34.25%, 24.98% and 16.13% for the basic process, and operating schemes, 1, 2, 3-P1 and 4-P1, respectively. For the operating schemes, 3-P2 and 4-P2,

the first-law process efficiencies increase to 32.17% and 28.11% and the
second-law process efficiencies to 25.58% and 17.31%, respectively, because
the hot water is considered to be usable outside the system. The
first-law and second-law process efficiencies of the overall system
decrease as the fraction of the digester gas allocated to the gas engine,
x, increases because the conversion ratio of the digester gas to work
is low, i.e., around 30%; the energy consumption and available energy
dissipation increase considerably as mentioned above.

The thermodynamic first-law incremental efficiencies of the
overall systems are 57.94%, 67.75%, 75.21% and 80.01%, and the second-
law incremental efficiencies of the overall systems are 24.80%, 30.12%,
33.00% and 34.65% for the operating schemes, 1, 2, 3 and 4, respectively.
As a whole, the energy loss associated with the effluent from the digester
tank is the substantial inefficiency for the first-law process efficiency,
while the available energy loss associated with the effluent and the
available energy dissipation in the gas engine subsystem are the main
inefficiencies for the second-law process efficiency. A high avail-
able energy dissipation gives rise to a relatively low second-law
incremental efficiency for each operating scheme. The mass, energy
and available energy flow diagrams are illustrated in Figs. 4, 5 and
6, respectively, for the operating scheme, 4-P2.

Optimization Study

To gain deeper insight into the system performance as it is affected
by the structural modification, the variation in the operating scheme,
the relative values of the digester gas and work form of energy pro-
duced, and the interaction among them, an optimization study has been
carried out. Specifically, the available energy content of the digester
gas directly supplied for off-site usage, the net work generated by

the gas engine for off-site usage and the available energy dissipation in the system are taken into account as objectives. For the operating schemes of the modified process, 3-P2 and 4-P2, the available energy content of the hot water from the gas engine for off-site usage is also considered.

The optimization problem posed here is stated as:

Maximizing the objective or profit function

$$J_0 = w_1 f_1(x) + w_2 f_2(x) - w_3 f_3(x) + w_4 f_4(x) \qquad (24)$$

subject to

$$0 \leq x \leq 1$$

where f_1 is the available energy content of the digester gas directly supplied for off-site usage, f_2 the available energy content of the hot water recovered from the gas engine subsystem for off-site usage, f_3 the available energy dissipation, f_4 the net work generated by the system for off-site usage and x the utilization ratio; it is defined as the fraction of the total digester gas, which is allocated to the gas engine. Note that w_1, w_2, w_3 and w_4 are the weighting coefficients, each representing the degree of importance of the corresponding objective to the decision maker; they can be interpreted as prices. f_1, f_2, and f_3 are the available energy contents of the process streams or the dissipations; for simplicity, therefore, it is assumed that

$$w_1 = w_2 = w_3 = 1,$$

and thus, equation (24) can be rewritten as

$$J = f_1(x) + f_2(x) - f_3(x) + wf_4(x) \qquad (25)$$

where w is the relative weighting coefficient. Considering that the work form of energy is at least as valuable as the available energy

content in the digester gas produced, w has been parametrically changed in such a way that its value is not less than 1; in fact, it has been varied parametrically between 1 and 6.

Because of the simplicity of the optimization problem posed, the exhaustive search has been employed. Table 10 contains the values of the objective function, J, for the basic process and for all the operating schemes of the modified process for different values of the relative weighting coefficient, w. These values are also plotted in Fig. 7; the region where the objective function, J, is not a monotonically increasing or decreasing function is elaborated in Fig. 8.

Figures 7 and 8 indicate that when w is less than 4.7, J decreases monotonically; it has the maximum value (optimal solution) at x=0, which corresponds to the basic process, and the minimum value (lowest profit) at x=1, which corresponds to operating scheme 4. When w is greater than 4.7 and less than 5.4, J is not a monotonic function and has the maximum value at x = 0 for w less than 4.9 and at x = 1 for w greater than 4.9. The trajectory of the minimum points is identified in Fig. 8 for operating scheme P2. When w is greater than 5.4, J increases monotonically; it has the maximum value at x = 1 and the minimum value at x = 0. Since a portion of the hot water generated in the system is discarded in operating scheme P1, the values of J are less than those for operating scheme P2 when x is greater than 0.4878, as illustrated by the dotted lines in both Figs. 7 and 8.

CONDLUDING REMARKS

The thermodynamic analysis and parametric optimization study have

been carried out for an anaerobic sludge digestion system. The energy

consumption, the available energy dissipation and the thermodynamic

first-law and second-law process and incremental efficiencies have

been evaluated. The procedure employed has enabled us to identify the sources

of thermodynamic inefficiency; the energy and available energy losses

associated with the effluent from the digester and the available energy

dissipation in the gas engine subsystem are the main inefficiencies in

the system.

The second-law efficiency has been found to be appreciably different

from the first-law efficiency, indicating the necessity of including both the

energy and available energy balances in process analysis and design. The

process efficiency has been found to be substantially different from the

incremental efficiency, indicating the necessity of considering both the

energy conservation and transformation in process analysis and design.

The approach employed in the optimization study is rather simple

in comparison with other approaches (see, e.g., Reistad and Gaggioli,

1980; Evans, 1980). Nevertheless, the information obtained from this

study should be useful in a preliminary or conceptual design of an anaerobic

digestion system of the type considered in this work.

NOMENCLATURE

A   = system A

$(A_{ex})_i$ = available energy input per unit time, J/sec or kcal/day

$(A_{ex})_{dis}$ = available energy dissipation per unit time, J/sec or kcal/day

$(A_{ex})_{e,d}$ = discarded portion of the available energy output per unit time, J/sec or kcal/day

$(A_{ex})_{e,u}$ = usable portion of the available energy output per unit time, J/sec or kcal/day

$(A_{ex})_\ell$ = available energy leakage per unit time, J/sec or kcal/day

$\{(A_{ex})_e\}_D$ = available energy transferred from system A to energy sinks per unit time, J/sec or kcal/day

$\{(A_{ex})_i\}_D$ = available energy transferred from energy sources to system A per unit time, J/sec or kcal/sec

E   = internal energy. J or kcal

e   = output streams

$(H_{av})_c$ = energy consumption per unit time, J/sec or kcal/day

$(H_{av})_{e,d}$ = discarded portion of the energy output per unit time, J/sec or kcal/day

$(H_{av})_{e,u}$ = usable portion of the energy output per unit time, J/sec or kcal/day

$(H_{av})_i$ = energy input per unit time, J/sec or kcal/day

$(H_{av})_\ell$ = energy leakage per unit time, J/sec or kcal/day

$\{(H_{av})_e\}_D$ = energy transferred from system A to energy sinks per unit time, J/sec or kcal/day

$\{(H_{av})_i\}_D$ = energy transferred from energy sources to system A per unit time, J/sec or kcal/day

$\bar{h}$ = partial molar enthalpy, J/kmol or kcal/kmol

$\bar{h}_0$ = partial molar enthalpy at the dead state, J/kmol or kcal/kmol

i   = input streams

J   = objective function

k   = material species

ℓ = leakage

$M_{e,d}$ = discarded part of mass output per unit time, kg/sec or kg/day

$M_{e,u}$ = usable part of mass output per unit time, kg/sec or kg/day

M_i = mass input per unit time, kg/sec or kg/day

M_ℓ = mass leakage per unit time, kg/sec or kg/day

Mw = molecular weight, kg/kmol

n = molar flow rate including both convective and diffusional flows, kmol/sec or kmol/day

P = pressure, atm

P_0 = pressure at the dead state, atm

$|Q_0|$ = heat loss to the environment per unit time, J/sec or kcal/day

$|Q_1|$ = heat transmitted from system M1 to system A per unit time, J/sec or kcal/day

$|Q_2|$ = heat transmitted from system A to system M2 per unit time, J/sec or kcal/day

S = entropy, J/K or kcal/K

s = specific entropy, J/kmol·K or kcal/kmol·K

s_0 = specific entropy at the dead state, J/kmol·K or kcal/kmol·K

T = temperature of system A, K

T_{m1} = temperature of system M1, K

T_{m2} = temperature of system M2, K

T_0 = temperature at the dead state, K

$U^2/2$ = specific kinetic energy, J/kmol or kcal/kmol

$|(W_x)_0|$ = work loss to the environment except that due to the expansion of the boundaries of system A per unit time, J/sec or kcal/day

$|W_1|$ = work supplied from the work source, system N1, to system A per unit time, J/sec or kcal/day

$|W_2|$ = work supplied from system A to the work source, system N2, per unit time, J/sec or kcal/day

w   = relative weighting coefficient

X_g = specific potential energy, J/kmol or kcal/kmol

x   = utilization ratio

GREEK

$\bar{\beta}$ = partial molar enthalpy relative to the dead state, J/kmol or kcal/kmol

$\bar{\beta}^0$ = specific chemical enthalpy, J/kmol or kcal/kmol

$\bar{\gamma}$ = partial molar entropy relative to the dead state, J/kmol·K or kcal/kmol·K

$\bar{\gamma}^0$ = specific chemical entropy, J/kmol·K or kcal/kmol·K

$\bar{\varepsilon}$ = partial molar exergy, J/kmol or kcal/kmol

$\bar{\varepsilon}^0$ = specific chemical exergy, J/kmol or kcal/kmol

η_m = mass utilization efficiency

$(\eta_1)_D$ = thermodynamic first-law incremental efficiency

$(\eta_1)_P$ = thermodynamic first-law process efficiency

$(\eta_2)_D$ = thermodynamic second-law incremental efficiency

$(\eta_2)_P$ = thermodynamic second-law process efficiency

σ = created entropy per unit time, J/K·sec or kcal/K·day

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Table 1. Flow rates and compositions of
influent and effluent.

	① Influent		② Effluent	
	(kg/day)	(wt%)	(kg/day)	(wt %)
Water	116,400	97.00	116,100	97.97
Total Solid	3,600	3.00	2,400	2.03
Total Flow Rate	120,000	100	118,500	100
Solid Components	(kg/day)	(wt%*)	(kg/day)	(wt%*)
C	1,314	36.50	657.0	27.41
H	192.6	5.35	78.3	3.27
N	156.6	4.35	156.6	6.53
O	900.0	25.00	468.0	19.53
Ash	1,036.8	28.80	1,036.8	43.26
Total	3,600	100	2,400	100

* Dry basis

Table 2. Components of the digester
gas and flue gas.

	(5) Digester Gas (wt %)	(8) Flue Gas (wt %)
CH_4	38.89	--
CO_2	57.58	21.41
H_2O (g)	3.53	11.37
N_2	--	67.22
Total	100	100

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Table 3. conditions, energy content and available energy content of each stream of the basic process.

	Flow Rate (kg/day)	T (K)	P (atm)	β (kcal/kg)	ϵ (kcal/kg)	H_{av} (10³ kcal/day)	A_{ex} (10³ kcal/day)
① Influent	120,000	298.15	1	112.5	114.2	13,500	13,700
② Effluent	118,540	308.15	1	60.55	52.39	7,178	6,210
③ Hot Water	39,430	368.15	1	70.00	7.122	2,760	280.8
④ Drained Water	39,430	333.15	1	35.00	1.907	1,380	75.19
⑤ Digester Gas	1,459	308.15	1	5,196	4,891	7,581	7,136

Note: $\beta = h - h_0$, $\epsilon = (h - h_0) - T_0(s - s_0)$.

Table 4. Conditions, energy content and available energy content of each stream of the modified process: operating scheme 1 with x = 0.25.

	Flow Rate (kg/day)	T (K)	p (atm)	β (kcal/kg)	ε (kcal/kg)	Π_av (10³ kcal/day)	A_ex (10³ kcal/day)
① Influent	120,000	298.15	1	112.5	114.2	13,500	13,700
② Effluent	118,540	308.15	1	60.55	52.39	7,178	6,210
③ Hot Water	19,210	368.15	1	70.00	7.122	1,345	136.8
④ Drained Water	21,230	333.15	1	35.00	1.907	743.1	40.49
⑤ Digester Gas	1,094	308.15	1	5,196	4,891	5,684	5,351
⑥ Digester Gas	365	308.15	1	5,196	4,891	1,897	1,785
⑦ Air	2,945	298.15	1	0	0	0	0
⑧ Flue Gas	3,310	473.15	1	104.8	45.01	349.1	149.0
⑨ Make-up Water	2,020	298.15	1	0	0	0	0
⑩ Hot Water	20,220	368.15	3	70.05	7.170	1,416	145.0
⑪ Hot Water	---	---	-	---	---	---	---
⑫ Recycled Water	18,200	333.15	5	35.10	2.004	638.8	36.47

Note: $\beta = h - h_0$, $\varepsilon = (h - h_0) - T_0(s - s_0)$.

Table 5. Conditions, energy content and available energy content of each stream of the modified process: operating scheme 2.

	Flow Rate (kg/day)	T (K)	P (atm)	β (kcal/kg)	ε (kcal/kg)	H_{av} (10^3 kcal/day)	A_{ex} (10^3 kcal/day)
① Influent	120,000	298.15	1	112.5	114.2	13,500	13,700
② Effluent	118,540	308.15	1	60.55	52.39	7,178	6,210
③ Hot Water	---	---	-	---	---	---	---
④ Drained Water	3,940	333.15	1	35.00	1.907	137.9	7.514
⑤ Digester Gas	747.3	308.15	1	5,196	4,891	3,883	3,655
⑥ Digester Gas	711.7	308.15	1	5,196	4,891	3,698	3,481
⑦ Air	5,746	298.15	1	0	0	0	0
⑧ Flue Gas	6,458	473.15	1	104.8	45.01	676.8	290.7
⑨ Make-up Water	3,940	298.15	1	0	0	0	0
⑩ Hot Water	39,430	368.15	3	70.05	7.170	2,762	282.7
⑪ Hot Water	---	---	-	---	---	---	---
⑫ Recycled Water	35,490	333.15	5	35.10	2.004	1,246	71.12

Note: $\beta = h - h_0$, $\varepsilon = (h - h_0) - T_0(s - s_0)$.

Table 6. Conditions, energy content and available energy content of each stream of the modified process: operating scheme 3 with x = 0.75.

		Flow Rate (kg/day)	T (K)	P (atm)	β (kcal/kg)	ε (kcal/kg)	$\bar{H}_{av}$ (10^3 kcal/day)	A_{ex} (10^3 kcal/day)
①	Influent	120,000	298.15	1	112.5	114.2	13,500	13,700
②	Effluent	118,540	308.15	1	60.55	52.39	7,178	6,210
③	Hot Water	---	---	-	---	---	---	---
④	Drained Water	3,940	333.15	1	35.00	1.907	137.9	7.514
⑤	Digester Gas	365	308.15	1	5,196	4,891	1,897	1,785
⑥	Digester Gas	1,094	308.15	1	5,196	4,891	5,686	5,351
⑦	Air	8,835	298.15	1	0	0	0	0
⑧	Flue Gas	9,930	473.15	1	104.8	45.01	1,041	446.9
⑨	Make-up Water	14,750	298.15	1	0	0	0	0
⑩	Hot Water	39,430	368.15	3	70.05	7.176	2,762	282.7
⑪	Hot Water	11,640	368.15	3	70.05	7.170	815.4	83.46
⑫	Recycled Water	35,490	333.15	5	35.10	2.004	1,246	71.12

Note: $\beta = h - h_0$, $\varepsilon = (h - h_0) - T_0 (s - s_0)$.

Table 7. Conditions, energy content and available energy content of each stream of the modified process: operating scheme 4.

	Flow Rate (kg/day)	T (K)	P (atm)	β (kcal/kg)	ε (kcal/kg)	H_{av} (10³ kcal/day)	A_{ex} (10³ kcal/day)
① Influent	120,000	298.15	1	112.15	114.2	13,500	13,700
② Effluent	118,540	308.15	1	60.55	52.39	7,178	6,210
③ Hot Water	---	---	-	---	---	---	---
④ Drained Water	3,940	333.15	1	35.00	1.907	137.9	7.514
⑤ Digester Gas	---	---	-	---	---	---	---
⑥ Digester Gas	1,459	308.15	1	5,196	4,891	7,581	7,136
⑦ Air	11,780	298.15	1	0	0	0	0
⑧ Flue Gas	13,240	473.15	1	104.8	45.01	1,388	595.9
⑨ Make-up Water	26,670	298.15	1	0	0	0	0
⑩ Hot Water	39,430	368.15	3	70.05	7.170	2,762	282.7
⑪ Hot Water	22,730	368.15	3	70.05	7.170	1,592	163.0
⑫ Recycled Water	35,490	333.15	5	35.10	2.004	1,246	71.12

Note: $\beta = h - h_0$, $\varepsilon = (h - h_0) - T_0(s - s_0)$.

Table 8. Work requirements and generations for the basic and modified processes.

		Basic Process	Modified Process			
			Scheme 1	Scheme 2	Scheme 3	Scheme 4
$\lvert w_{P1} \rvert$,	$\dfrac{10^3 \text{ kcal}}{\text{day}}$	8.298	8.298	8.298	8.298	8.298
	$\left(\dfrac{\text{kwh}}{\text{day}}\right)$	(9.649)	(9.649)	(9.649)	(9.649)	(9.649)
$\lvert w_{P2} \rvert$,	$\dfrac{10^3 \text{ kcal}}{\text{day}}$	2.727	1.328	---	---	---
	$\left(\dfrac{\text{kwh}}{\text{day}}\right)$	(3.171)	(1.545)			
$\lvert w_{P3} \rvert$,	$\dfrac{10^3 \text{ kcal}}{\text{day}}$	---	2.571	4.908	4.908	4.908
	$\left(\dfrac{\text{kwh}}{\text{day}}\right)$		(2.927)	(5.707)	(5.707)	(5.707)
$\lvert w_{P4} \rvert$,	$\dfrac{10^3 \text{ kcal}}{\text{day}}$	---	0.2794	0.5449	2.040	3.689
	$\left(\dfrac{\text{kwh}}{\text{day}}\right)$		(0.3249)	(0.6336)	(2.372)	(4.289)
$\lvert w_m \rvert$,	$\dfrac{10^3 \text{ kcal}}{\text{day}}$	39.56	39.56	39.56	39.56	39.56
	$\left(\dfrac{\text{kwh}}{\text{day}}\right)$	(46.00)	(46.00)	(46.00)	(46.00)	(46.00)
$\lvert w_e \rvert$,	$\dfrac{10^3 \text{ kcal}}{\text{day}}$	---	569.4	1,109	1,705	2,274
	$\left(\dfrac{\text{kwh}}{\text{day}}\right)$		(662.1)	(1,290)	(1,983)	(2,644)
$\lvert w_x \rvert$,	$\dfrac{10^3 \text{ kcal}}{\text{day}}$	---	517.4	1,056	1,630	2,218
	$\left(\dfrac{\text{kwh}}{\text{day}}\right)$		(601.6)	(1,228)	(1,919)	(2,579)

Table 9. Energy consumptions, available energy dissipations and efficiencies of the basic and modified processes.

		$\Sigma(H_{av})_c$ ($\frac{10^3 \text{ kcal}}{\text{day}}$)	z^a (%)	$\Sigma(A_{ex})_{dis}$ ($\frac{10^3 \text{ kcal}}{\text{day}}$)	z^b (%)	$(\eta_1)_{P1}$ (%)	$(\eta_1)_{P2}$ (%)	$(\eta_2)_{P1}$ (%)	$(\eta_2)_{P2}$ (%)	$(\eta_1)_D$ (%)	$(\eta_2)_D$ (%)
Basic Process		171.6	100	610.2	100	46.48	–	50.80	–	88.01	–
Scheme 1	Digester	171.8	45.74	610.5	38.92	50.38	–	51.11	–	87.99	–
	Gas Engine	203.8	54.26	958.3	61.08	28.31	–	39.22	–	86.90	41.43
	Overall	375.6	100	1,569	100	41.63	–	42.25	–	57.94	24.80
Scheme 2	Digester	171.8	30.22	606.9	24.50	54.10	–	51.35	–	87.99	–
	Gas Engine	396.7	69.78	1,870	75.50	28.28	–	39.17	–	86.87	41.39
	Overall	568.5	100	2,477	100	36.45	–	34.25	–	67.75	41.12
Scheme 3	Digester	171.9	21.96	610.8	17.37	54.10	54.10	51.35	51.35	87.99	–
	Gas Engine	611.0	78.04	2,906	82.63	64.42	76.16	36.65	38.18	86.85	40.77
	Overall	782.9	100	3,517	100	26.16	32.17	24.98	25.58	75.12	33.00
Scheme 4	Digester	171.9	17.42	610.8	13.55	54.10	54.10	51.35	51.35	87.99	–
	Gas Engine	814.7	82.58	3,896	86.45	57.03	75.06	35.46	37.72	86.85	40.47
	Overall	986.6	100	4,507	100	16.37	28.11	16.13	17.31	80.01	34.65

Modified Process

a) Percentage contribution to the total energy consumption.
b) Percentage contribution to the total available energy dissipation.

Table 10. Objective function, J, for the basic and modified processes for different values of the relative weighting coefficient, w.

	Basic Process	Operating Scheme of the Modified Process					
		1	2	3-P1	3-P2	4-P1	4-P2
f_1	7,136	5,351	3,655	1,785	1,785	0	0
f_2	0	0	0	0	83.46	0	163
f_3	610.2	1,569	2,477	3,517	3,517	4,507	4,507
f_4	0	517.4	1,056	1,650	1,650	2,218	2,218
w=1.0	6,526	4,299	2,234	-81	1	-2,289	-2,126
2.0	6,526	4,817	3,290	1,568	1,651	-71	92
3.0	6,526	5,334	4,346	3,218	3,301	2,147	2,310
4.0	6,526	5,851	5,402	4,368	4,951	4,365	4,528
4.5	6,526	6,110	5,930	5,693	5,776	5,474	5,637
4.6	6,526	6,162	6,036	5,858	5,941	5,696	5,859
4.7	6,526	6,214	6,141	6,023	6,106	5,918	6,081
4.75	6,526	6,239	6,194	6,106	6,189	6,029	6,192
4.8	6,526	6,265	6,247	6,188	6,271	6,139	6,302
4.9	6,526	6,317	6,352	6,352	6,436	6,361	6,524
5.0	6,526	6,369	6,458	6,518	6,601	6,583	6,746
5.1	6,526	6,421	6,564	6,683	6,766	6,805	6,968
5.2	6,526	6,472	6,669	6,848	6,931	7,027	7,190
5.3	6,526	6,524	6,775	7,013	7,096	7,248	7,411
5.4	6,526	6,575	6,880	7,173	7,261	7,470	7,633
6.0	6,526	6,886	7,514	8,163	8,251	8,801	8,964
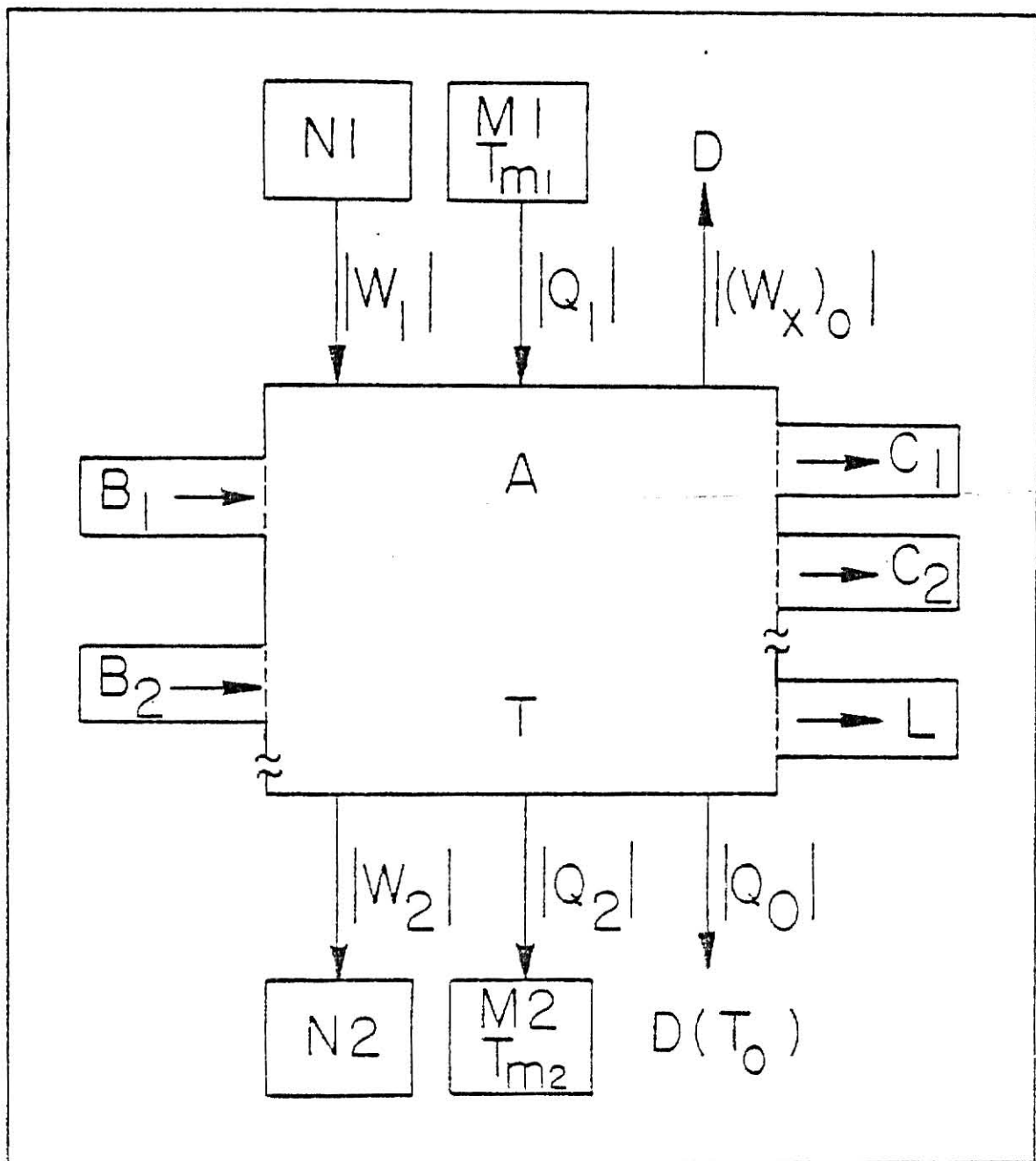
Fig. 1. Schematic diagram of an open flow system.
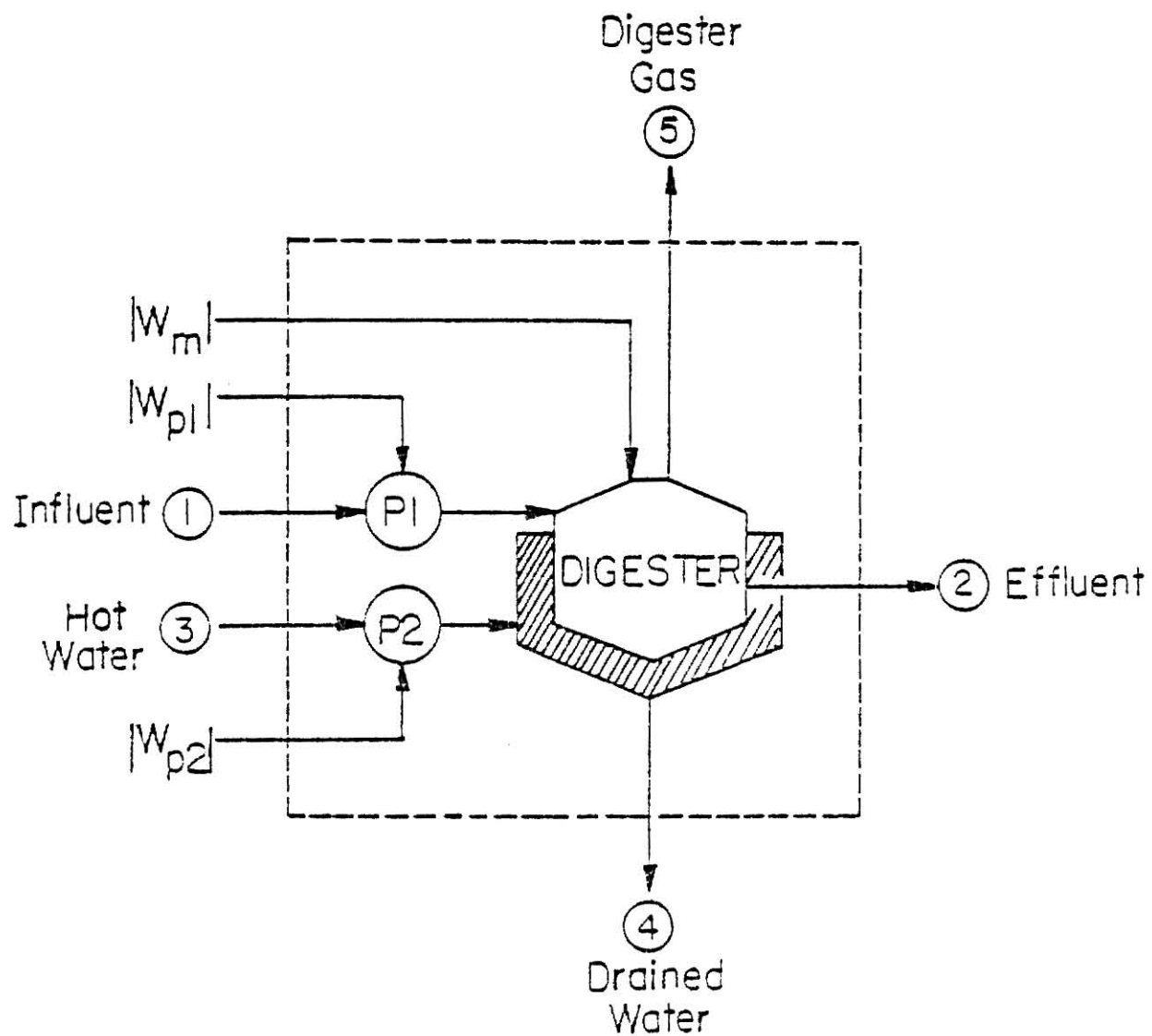
Fig. 2.   Schematic diagram of the basic process of the digestion system.
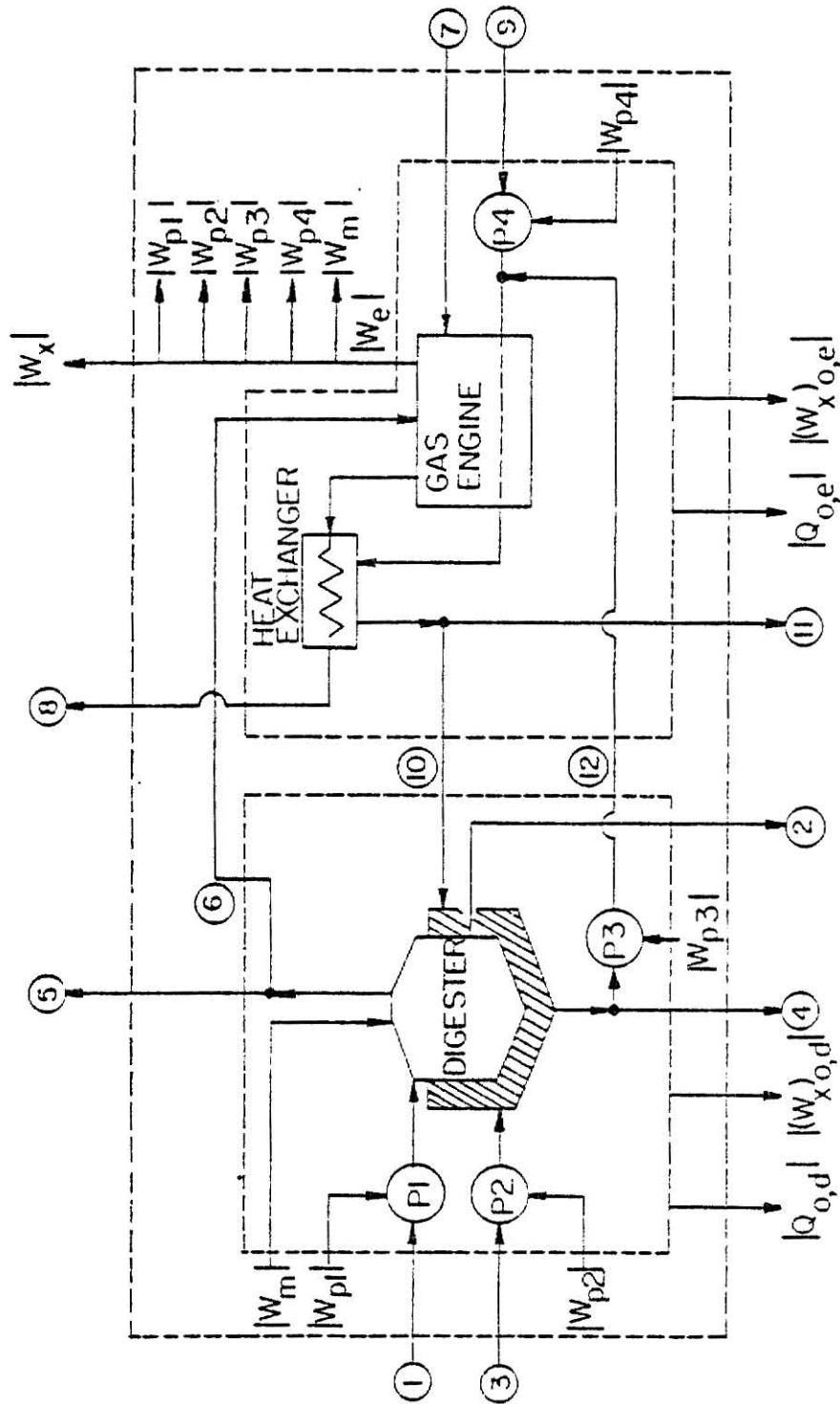
Fig. 3. Schematic diagram of the modified process of the digestion system:
1. Influent, 2. Effluent, 3. Hot water, 4. Drained Water,
5. Digester Gas, 6. Digester Gas, 7. Air, 8. Flue Gas,
9. Make-up Water, 10. Hot Water, 11. Hot Water, 12. Recycled Water.
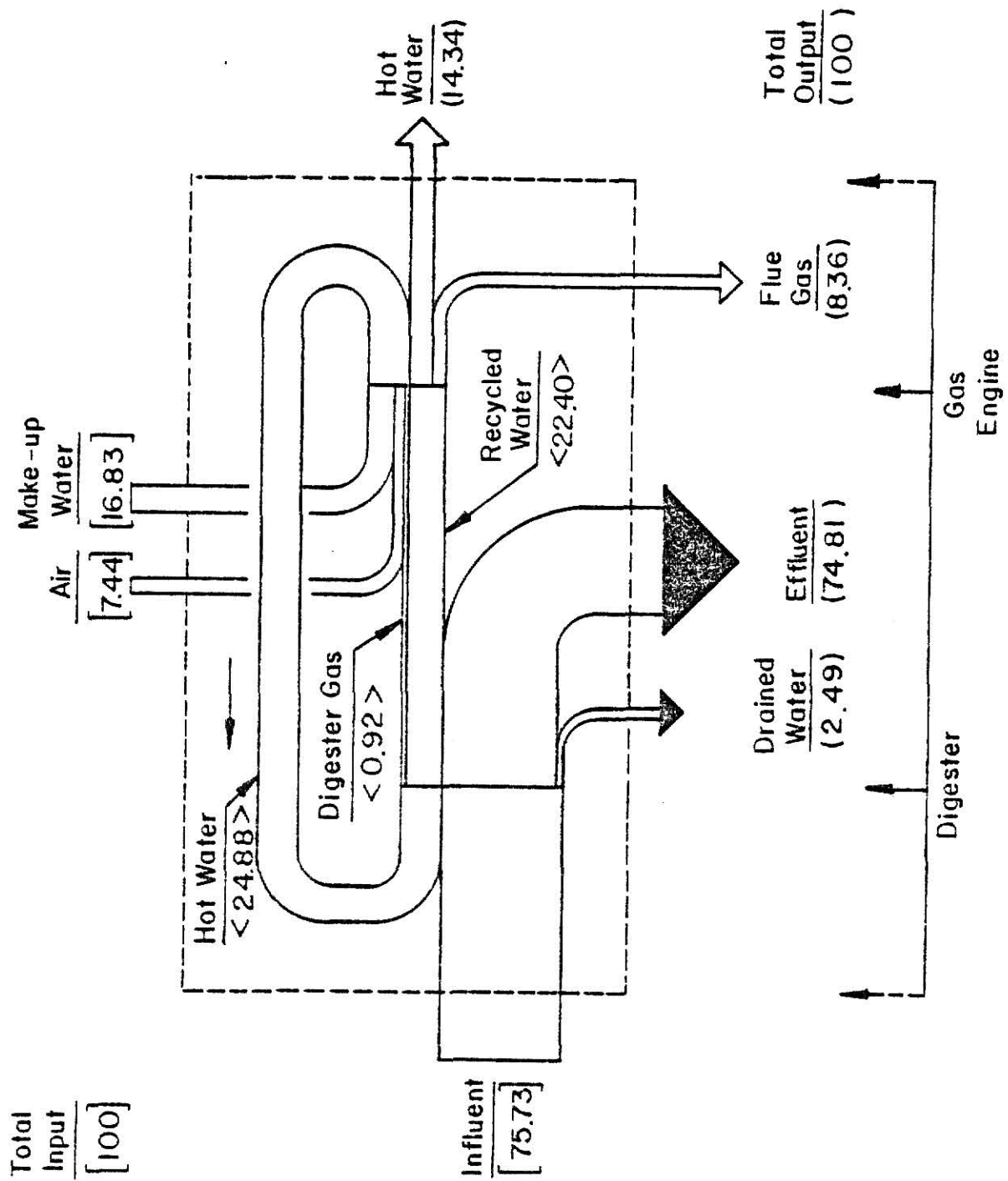
Fig. 4. Mass flow diagram for operating scheme 4-P2 of the anaerobic digestion system.
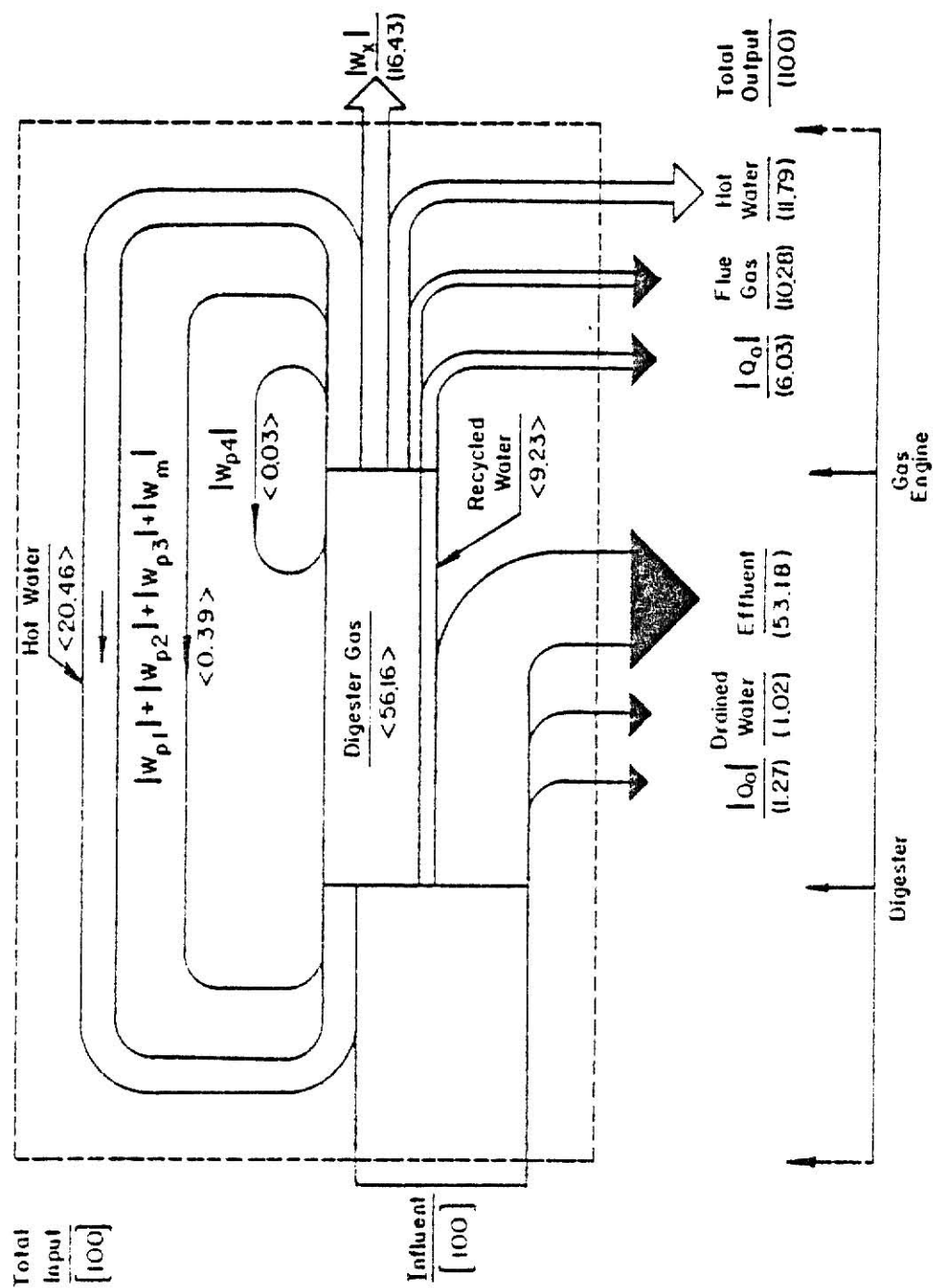
Fig. 5. Energy flow diagram for operating scheme 4-P2 of the anaerobic digestion system.
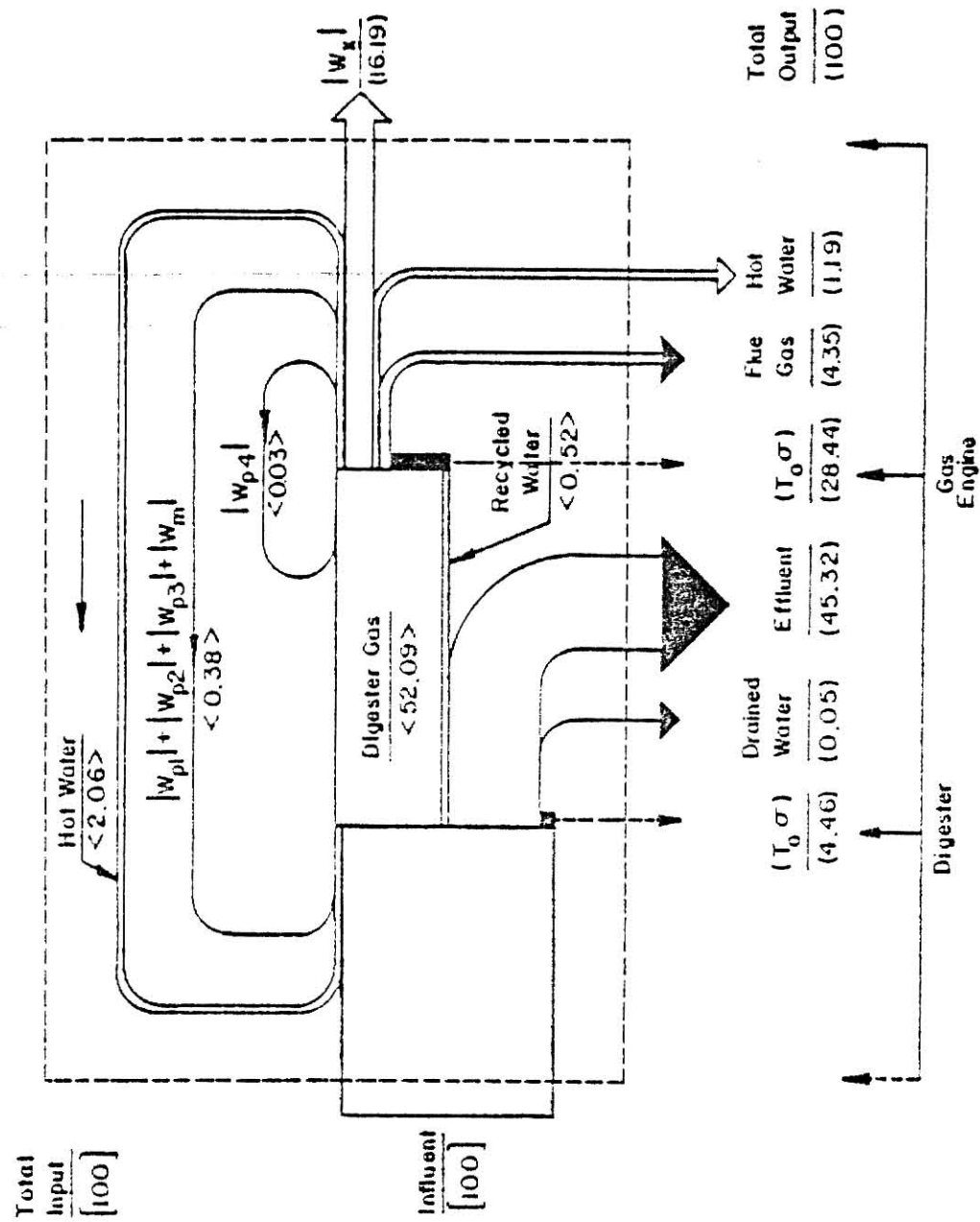
Fig. 6. Available energy flow diagram for operating scheme 4-P2 of the anaerobic digestion system.
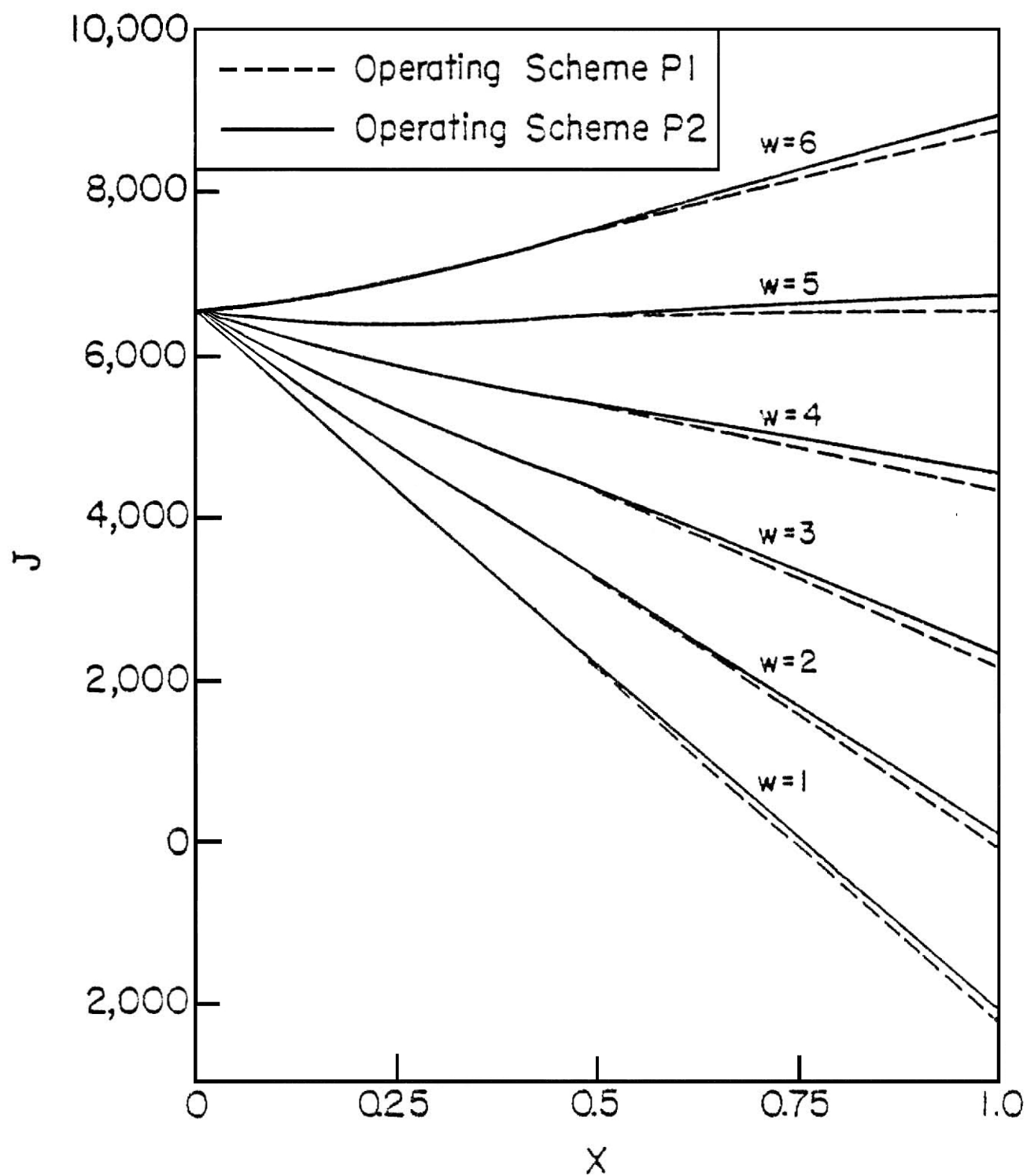
Fig. 7. Objective function, J, as a function of the utilization ratio, x.
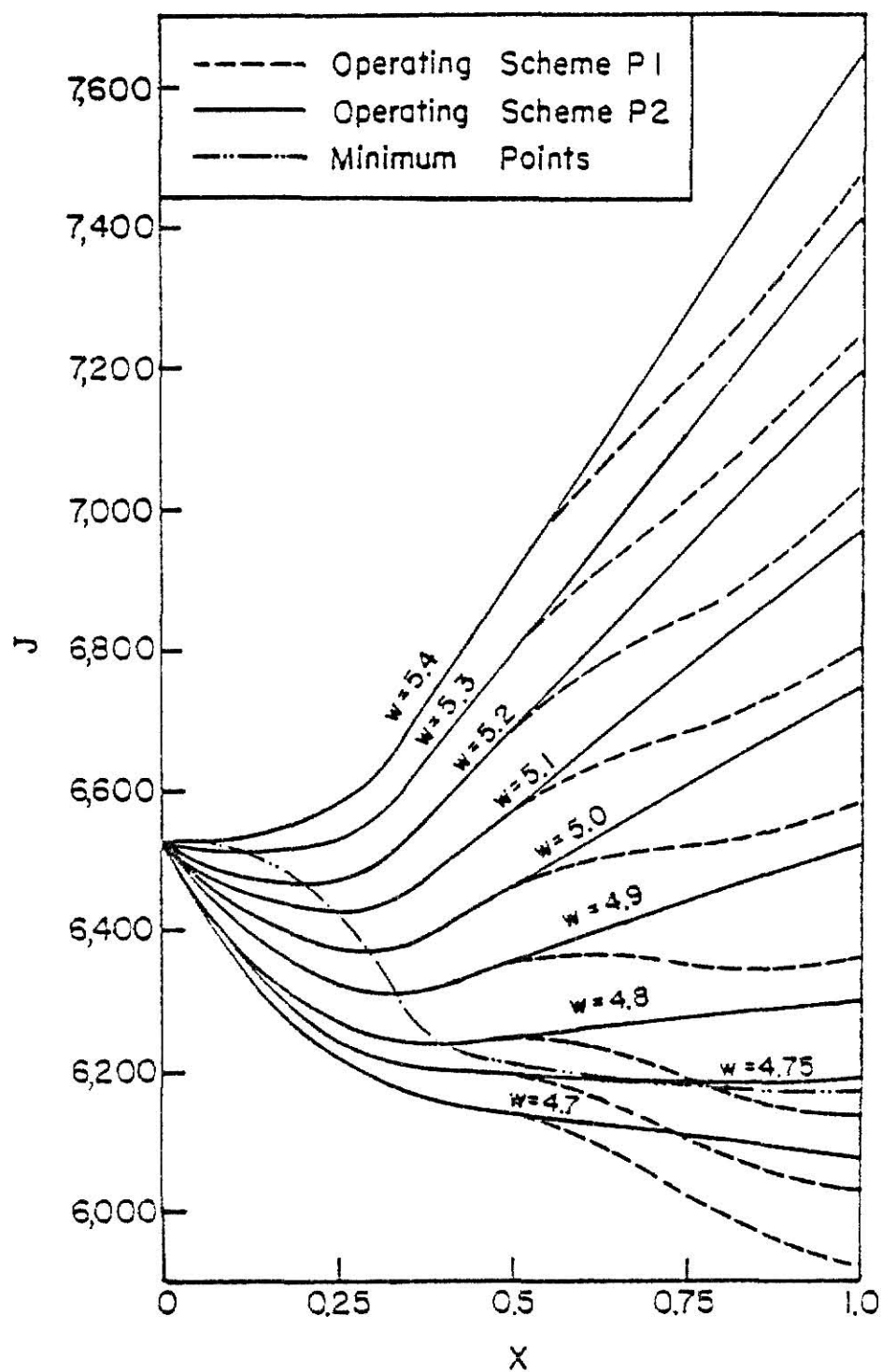
Fig. 8. Objective function, J, as a function of the
utilization ratio, x; J has the minimum
point between x = 0 and 1.

CHAPTER 7

CONCLUSION AND RECOMMENDATION

CONCLUSION AND RECOMMENDATION

The single axiom approach of thermodynamics has been reviewed, and a systematic procedure for thermodynamic system analysis has been developed. It has been shown that the laws and general relations of classical thermodynamics can be deduced from a single axiom which is called the law of stable equilibrium. Thus, classical thermodynamics is seen as an extension of the concepts of stable equilibrium and of the uniqueness of the stable state. The single axiom approach indicates directly the existence of irreversibility of a process system; consequently, it is naturally followed by the concept of available energy.

The procedure of system analysis developed enables us to determine the efficiencies of a process system from the viewpoints of mass utilization (mass balance), thermodynamic first law (energy balance) and thermodynamic second law (available energy balance). The procedure also enables us to identify the nature and location of the thermodynamic inefficiency and irreversibility of the system. Its use has been illustrated with several examples, namely, a counter-current heat exchanger system, a biomass pyrolysis system and an anaerobic digestion system.

In practice, the installation of the energy or material recovery units in a system is counter-balanced by an increase in the capital and operating costs. Therefore, to optimize the design, the costs and other constraints need be taken into account, and whenever possible, a detailed trade-off analysis among the different criteria should be carried out.

APPENDIX A. DERIVATION OF THE MASS, ENERGY, ENTROPY AND
AVAILABLE ENERGY BALANCES FOR AN UNSTEADY-STATE OPEN FLOW SYSTEM

The mass, energy, entropy and available energy balances are
rigorously derived for an unsteady-state open flow system. The first
and second laws of thermodynamics lead to the energy and entropy
balances, respectively. Provided that the energy and entropy contents
of materials involved are measured relative to the dead state, the
combination of these two balances gives rise to the available energy
balance, and the concepts and definitions of essergy and exergy.

An overall system illustrated in Fig. A-1 is considered for the
purpose of writing explicitly the balances. The overall system contains
an unsteady-state open flow system with multiple input and output
streams (system A), a heat source at temperature T_{m1} (system M1), a heat
sink at temperature T_{m2} (system M2), a work source (system N1), a work
sink (system N2) and the surroundings at temperature T_0 and pressure
P_0 (D).

MASS BALANCE

The law of mass conservation can be expressed for system A as

$$\begin{bmatrix} \text{accumulation} \\ \text{of mass in} \\ \text{system A} \end{bmatrix} = \begin{bmatrix} \text{mass input} \\ \text{to} \\ \text{system A} \end{bmatrix} - \begin{bmatrix} \text{mass output} \\ \text{from} \\ \text{system A} \end{bmatrix}$$

$$- \begin{bmatrix} \text{leakage} \\ \text{from} \\ \text{system A} \end{bmatrix} \tag{A-1}$$

This expression can be rewritten for system A, transforming from state 1
at t = 0 to state 2 at t = t, as

$$\left\{ M_{A2}(t) - M_{A1} \right\}$$

$$= \int_0^t \left\{ \int_{\Omega_i} \sum_k \left[(Mw)_k \, j_k(t,a) \right] \, da_i \right\} \, dt$$

$$- \int_0^t \left\{ \int_{\Omega_e} \sum_k \left[(Mw)_k \, j_k(t,a) \right] \, da_e \right\} \, dt$$

$$- \int_0^t \left\{ \int_{\Omega_\ell} \sum_k \left[(Mw)_k \, j_k(t,a) \right] da_\ell \right\} \, dt \qquad \text{(A-2)}$$

where

M_A = mass in system A

Mw = molecular weight

j = molar flux (rate of flow per unit surface)

Ω = control surface which the matter crosses

a = unit area of Ω

and the subscripts stands for:

i = input streams

e = output streams

ℓ = leakage streams

k = material species

By introducing the molar flow rate including both the convective and diffusional flows, which is expressed as

$$n_k = \int_\Omega j_k \, da, \qquad \text{(A-3)}$$

equation (A-2) can be rewritten as

$$\left\{ M_{A2}(t) - M_{A1} \right\}$$

$$= \sum_i \left\{ \int_0^t \sum_k [(Mw)_k n_k(t)] \ dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(Mw)_k n_k(t) \ dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(Mw)_k n_k(t)] \ dt \right\}_\ell \qquad (A\text{-}4)$$

ENERGY BALANCE

Applying the first law of thermodynamics to system A, we have

$$\begin{bmatrix} \text{accumulation} \\ \text{of energy in} \\ \text{system A} \end{bmatrix} = \begin{bmatrix} \text{energy input} \\ \text{to} \\ \text{system A} \end{bmatrix} - \begin{bmatrix} \text{energy output} \\ \text{from} \\ \text{system A} \end{bmatrix}$$
$$- \begin{bmatrix} \text{energy loss} \\ \text{from} \\ \text{system A} \end{bmatrix} \qquad (A\text{-}5)$$

The energy loss from system A includes the energy loss associated with material leakage, and heat and work losses through the walls of the system to the surroundings. This expression can be written for the time interval considered as (see, e.g., Keenan, 1941; Hatsopoulos and Keenan, 1965; Denbigh, 1971)

$$\left\{ E_{A2}(t) - E_{A1} \right\}$$

$$= \int_0^t \left\{ \int_{\Omega_i} \sum_k [(\overline{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \ j_k(t,a)] \ da_i \right\} \ dt$$

$$+ \left\{ \int_0^t |Q_1(t)| \ dt + \int_0^t |W_1(t)| \ dt \right\}$$

$$- \int_0^t \left\{ \int_{\Omega_e} \sum_k \left[(\overline{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k j_k(t,a) \right] da_e \right\} dt$$

$$- \left\{ \int_0^t |Q_2(t)| \, dt + \int_0^t |W_2(t)| \, dt \right\}$$

$$- \int_0^t \left\{ \int_{\Omega_\ell} \sum_k \left[(\overline{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k j_k(t,a) \right] da_\ell \right\} dt$$

$$- \left\{ \int_0^t |Q_0(t)| \, dt + \int_0^t |W_0(t)| \, dt \right\} \tag{A-6}$$

where

E_A = total internal energy of system A including kinetic energy, potential energy, etc.

$\overline{h}$ = partial molar enthalpy

gx = specific potential energy

$\dfrac{u^2}{2}$ = specific kinetic energy

$|Q_1|$ = heat transmitted from the heat source, system M1, to system A per unit time

$|Q_2|$ = heat transmitted from system A to the heat sink, system M2, per unit time

$|Q_0|$ = heat loss through the walls of system A to the surroundings per unit time

$|W_1|$ = work supplied from the work source, system N1, to system A per unit time

$|W_2|$ = work supplied from system A to the work sink, system N2, per unit time

$|W_0|$ = work loss through the walls of system A to the surroundings per unit time

By applying equation (A-3), this expression can be rewritten as

$$\left\{ E_{A2}(t) - E_{A1} \right\}$$

$$= \left\{ \sum_i \left[\int_0^t \sum_k \left(\bar{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots \right)_k n_k(t)\ dt \right]_i \right.$$

$$\left. + \int_0^t |Q_1(t)|\ dt + \int_0^t |W_1(t)|\ dt \right\}$$

$$- \left\{ \sum_e \left[\int_0^t \sum_k \left(\bar{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots \right)_k n_k(t)\ dt \right]_e \right.$$

$$\left. + \int_0^t |Q_2(t)|\ dt + \int_0^t |W_2(t)|\ dt \right\}$$

$$- \left\{ \sum_\ell \left[\int_0^t \sum_k \left(\bar{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots \right)_k n_k(t)\ dt \right]_\ell \right.$$

$$\left. + \int_0^t |Q_0(t)|\ dt + \int_0^t |W_0(t)|\ dt \right\} \tag{A-7}$$

The work, $|W|$, can be expressed in terms of not only mechanical work, which consists of tangential (rotating) and perpendicular (reciprocating) works, but also electric work, magnetic work, etc. Therefore, we have

$$|W| = |W_p| + |W_t| + |W_{elec}| + |W_{mag}| + \ldots$$

or

$$|W| = |W_p| + |W_x| \tag{A-8}$$

where

$$|W_x| = |W_t| + |W_{elec}| + |W_{mag}| + \ldots$$

$$|W_p| = \text{perpendicular work}$$

$$|W_t| = \text{tangential work}$$

$$|W_{elec}| = \text{electric work}$$

$$|W_{mag}| = \text{magnetic work}$$

Similarly, the work loss to the surroundings can be expressed as

$$|W_0| = |(W_P)_0| + |(W_x)_0| \qquad\qquad (A-9)$$

where

$$|(W_x)_0| = |(W_t)_0| + |(W_{elec})_0| + |(W_{mag})_0| + \ldots$$

and $|(W_P)_0|$ is the work loss due to expansion of the boundary of

system A, which is expressed as

$$\int_0^t |(W_P)_0(t)| \, dt = P_0(V_{A2} - V_{A1}) \qquad\qquad (A-10)$$

where P_0 is the pressure of the environment and V_A the volume of system A. The work and volume terms, appearing in equations (A-8) through (A-10) are, in general, functions of time. Substitution of equations (A-9) and (A-10) into equation (A-7) gives, after rearrangement,

$$[E_{A2}(t) - E_{A1}] + P_0[V_{A2}(t) - V_{A1}]$$

$$= \sum_i \left[\int_0^t \sum_k \left(\overline{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots \right)_k n_k(t) \, dt \right]_i$$

$$- \sum_e [\int_0^t \sum_k (\overline{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t) \, dt]_e$$

$$- \sum_\ell [\int_0^t \sum_k (\overline{h}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t) \, dt]_\ell$$

$$+ \int_0^t [|Q_1(t)| - |Q_2(t)| - |Q_0(t)|] \, dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)| - |(W_x)_0(t)|] \, dt \qquad \text{(A-11)}$$

Suppose that all the systems under consideration are at the dead state, where the systems are in equilibrium with the surroundings as regards pressure, temperature, compositions, electricity, magnetism, etc., and thus, no heat or work is transferred between system A and any one of other systems or the surroundings. We may, however, imagine the material streams entering or leaving system A reversiblly as a limiting process; this gives rise to the indefinitely slow expansion of the boundary of system A under an unsteady-state condition, which results in work done against the surroundings. For this process at the dead state, the energy balance can be written as

$$[(E_0)_{A2}(t) - (E_0)_{A1}]$$

$$= \sum_i [\int_0^t \sum_k (\overline{h}_0)_k(t) \, n_k(t) \, dt]_i$$

$$- \sum_e [\int_0^t \sum_k (\overline{h}_0)_k(t) \, n_k(t) \, dt]_e$$

$$- \sum_\ell [\int_0^t \sum_k (\overline{h}_0)_k \, n_k(t) \, dt]_\ell - \int_0^t |(W_{0,P})_0(t)| \, dt \qquad \text{(A-12)}$$

where subscript 0 inside the brackets denotes the dead state and

$|(W_{0,P})_0(t)|$ is the reversible expansion work at the dead state expressed as

$$\int_0^t |(W_{0,P})_0(t)| \ dt = P_0[(V_0)_{A2}(t) - (V_0)_{A1}] \qquad (A-13)$$

Substitution of this expression into equation (A-12) gives

$$[(E_0)_{A2}(t) - (E_0)_{A1}] + P_0[(V_0)_{A2}(t) - (V_0)_{A1}]$$

$$= \sum_i [\int_0^t \sum_k (\overline{h}_0)_k(t) \ n_k(t) \ dt]_i$$

$$- \sum_e [\int_0^t \sum_k (\overline{h}_0)_k(t) \ n_k(t) \ dt]_e$$

$$- \sum_\ell [\int_0^t \sum_k (\overline{h}_0)_k(t) \ n_k(t) \ dt]_\ell \qquad (A-14)$$

Subtracting each side of equation (A-14) from that of equation (A-11), we have

$$[E_{A2}(t) - E_{A1}] - [(E_0)_{A2}(t) - (E_0)_{A1}]$$

$$+ P_0[V_{A2}(t) - V_{A1}] - P_0[(V_0)_{A2}(t) - (V_0)_{A1}]$$

$$= \sum_i \left\{ \int_0^t \sum_k [(\overline{h}(t) - \overline{h}_0(t)) + gx(t) + \frac{u(t)^2}{2} + \ldots]_k \ n_k(t) \ dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(\overline{h}(t) - \overline{h}_0(t)) + gx(t) + \frac{u(t)^2}{2} + \ldots]_k \ n_k(t) \ dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(\overline{h}(t) - \overline{h}_0(t)) + gx(t) + \frac{u(t)^2}{2} + \ldots]_k \ n_k(t) \ dt \right\}_\ell$$

$$+ \int_0^t [|Q_1(t)| - |Q_2(t)| - |Q_0(t)|] \ dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)| - |(W_x)_0(t)|] \ dt \qquad (A-15)$$

By defining the partial molar enthalpy relative to the dead state as

$$\overline{\beta} \equiv \overline{h} - \overline{h}_0 \qquad (A\text{-}16)$$

equation (A-15) becomes

$$[E_{A2}(t) - E_{A1}] - [(E_0)_{A2}(t) - (E_0)_{A1}]$$
$$+ P_0[V_{A2}(t) - V_{A1}] - P_0[(V_0)_{A2}(t) - (V_0)_{A1}]$$

$$= \sum_i \left\{ \int_0^t \sum_k [(\overline{\beta}(t) + gx(t) + \frac{u(t)^2}{2} + \dots)_k n_k(t)]\, dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(\overline{\beta}(t) + gx(t) + \frac{u(t)^2}{2} + \dots)_k n_k(t)]\, dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(\overline{\beta}(t) + gx(t) + \frac{u(t)^2}{2} + \dots)_k n_k(t)]\, dt \right\}_\ell$$

$$+ \int_0^t [|Q_1(t)| - |Q_2(t)| - |Q_0(t)|]\, dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)| - |(W_x)_0(t)|]\, dt \qquad (A\text{-}17)$$

This is the expression of the energy balance for an unsteady-state open flow system.

ENTROPY BALANCE

The principle of the increase of entropy states (see, e.g., Keenan, 1941): "The entropy of an isolated system increases or in the limit remains constant." We can, therefore, write

$$(\Delta S)_{iso} \geq 0 \qquad (A\text{-}18)$$

where subscript iso stands for the isolated system. It is often convenient to convert this relation into an equality by introducting a non-negative quantity, σ; for a time interval considered, we may write (see, e.g. Denbigh, 1956)

$$(\Delta S)_{iso} = \int_0^t \sigma(t) \, dt \qquad \text{(A-19)}$$

where σ is understood as the rate of entropy created in the isolated system. Thus, the entropy balance around the isolated overall system shown in Fig. A-1 can be expressed as (see, e.g., Denbigh, 1956; Haywood, 1974).

[created entropy in the isolated system]

= [change in entropy in system A (ΔS_A)]

+ [change in entropy in system B (ΔS_B)]

+ [change in entropy in system C (ΔS_C)]

+ [change in entropy in system L (ΔS_L)]

+ [change in entropy in system M1 (ΔS_{M1})]

+ [change in entropy in system M2 (ΔS_{M2})]

+ [change in entropy in system D (ΔS_D)]   (A-20)

and each term in the right-hand side can be written as follows:

$$\Delta S_A = S_{A2}(t) - S_{A1}$$

$$\Delta S_B = - \int_0^t \left\{ \int_{\Omega_i} \sum_k [\bar{s}_k(t) \, j_k(t,a)] \, da_i \right\} dt$$

$$\Delta S_C = \int_0^t \left\{ \int_{\Omega_e} \sum_k [\bar{s}_k(t) \, j_k(t,a)] \, da_e \right\} dt$$

$$\Delta S_L = \int_0^t \left\{ \int_{\Omega_\ell} \sum_k [\bar{s}_k(t) \, j_k(t,a)] \, da_\ell \right\} dt$$

$$\Delta S_{M1} = - \int_0^t \frac{|Q_1(t)|}{T_{m1}} \, dt$$

$$\Delta S_{M2} = \int_0^t \frac{|Q_2(t)|}{T_{m2}} \, dt$$

$$\Delta S_D = \int_0^t \frac{|Q_0(t)|}{T_0} \, dt$$

where

T_{m1} = temperature of the heat source, system M1

T_{m2} = temperature of the heat sink, system M2

T_0 = temperature of the surroundings.

Note that ΔS_B, ΔS_C or ΔS_L corresponds respectively, to the change in entropy accompanied by the migration of material between system A and system B, C or L. Substitution of the corresponding expressions into equation (A-20) gives

$$\int_0^t \sigma(t)\, dt = [S_{A2}(t) - S_{A1}]$$

$$- \int_0^t \left\{ \int_{\Omega_i} \sum_k [\bar{s}_k(t)\, j_k(t,a)]\, da_i \right\} dt$$

$$+ \int_0^t \left\{ \int_{\Omega_e} \sum_k [\bar{s}_k(t)\, j_k(t,a)]\, da_e \right\} dt$$

$$+ \int_0^t \left\{ \int_{\Omega_\ell} \sum_k [\bar{s}_k(t)\, j_k(t,a)]\, da_\ell \right\} dt$$

$$+ \int_0^t \left[- \frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0}\right] dt \quad \text{(A-21)}$$

By using equation (A-3), this expression can be rewritten as

$$\int_0^t \sigma(t)\, dt = [S_{A2}(t) - S_{A1}]$$

$$- \sum_i \left\{ \int_0^t \sum_k [\bar{s}_k(t)\, n_k(t)]\, dt \right\}_i$$

$$+ \sum_e \left\{ \int_0^t \sum_k [\bar{s}_k(t)\, n_k(t)]\, dt \right\}_e$$

$$+ \sum_\ell \left\{ \int_0^t \sum_k [\bar{s}_k(t)\, n_k(t)]\, dt \right\}_\ell$$

$$+ \int_0^t [- \frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0}] \, dt \quad \text{(A-22)}$$

Similar to the energy balance, considering the overall system at the dead state, where the process streams are imagined to occur reversibly, we have

$$\sigma = 0$$

and thus, the entropy balance becomes

$$0 = [(S_0)_{A2}(t) - (S_0)_{A1}]$$

$$- \sum_i \left\{ \int_0^t \sum_k [(\overline{s}_0)_k(t) \, n_k(t)] \, dt \right\}_i$$

$$+ \sum_e \left\{ \int_0^t \sum_k [(\overline{s}_0)_k(t) \, n_k(t)] \, dt \right\}_e$$

$$+ \sum_\ell \left\{ \int_0^t \sum_k [(\overline{s}_0)_k(t) \, n_k(t)] \, dt \right\}_\ell \quad \text{(A-23)}$$

where subscript 0 denotes the dead state.

Subtracting each side of equation (A-23) from that of equation (A-22), we have

$$\int_0^t \sigma(t) \, dt = [S_{A2}(t) - S_{A1}] - [(S_0)_{A2}(t) - (S_0)_{A1}]$$

$$- \sum_i \left\{ \int_0^t \sum_k [\overline{s}(t) - (\overline{s}_0)(t)]_k \, n_k \, dt \right\}_i$$

$$+ \sum_e \left\{ \int_0^t \sum_k [\overline{s}(t) - (\overline{s}_0)(t)]_k \, n_k \, dt \right\}_e$$

$$+ \sum_\ell \left\{ \int_0^t \sum_k [\overline{s}(t) - (\overline{s}_0)(t)]_k \, n_k \, dt \right\}_\ell$$

$$+ \int_0^t [- \frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0}] \, dt \quad \text{(A-24)}$$

By defining

$$\overline{\gamma} \equiv \overline{s} - \overline{s}_0 \quad , \tag{A-25}$$

equation (A-24) reduces to

$$\int_0^t \sigma(t) \, dt = [S_{A2}(t) - S_{A1}] - [(S_0)_{A2}(t) - (S_0)_{A1}]$$

$$- \sum_i \left\{ \int_0^t \sum_k [\overline{\gamma}_k(t) \, n_k(t)] \, dt \right\}_i$$

$$+ \sum_e \left\{ \int_0^t \sum_k [\overline{\gamma}_k(t) \, n_k(t)] \, dt \right\}_e$$

$$+ \sum_\ell \left\{ \int_0^t \sum_k [\overline{\gamma}_k(t) \, n_k(t)] \, dt \right\}_\ell$$

$$+ \int_0^t [- \frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0}] \, dt \tag{A-26}$$

This is the expression of the entropy balance relative to the dead state for an unsteady-state open flow system.

AVAILABLE ENERGY BALANCE

Combination of the energy balance, equation (A-17), and the entropy balance, equation (A-26), gives rise to (see, e.g., Denbigh, 1956, 1971; Szargut and Petela, 1975; Riekert, 1974; Gaggioli and Petit, 1977; Fan and Shieh, 1980)

$$\left\{ [E_{A2}(t) - E_{A1}] - [(E_0)_{A2}(t) - (E_0)_{A1}] \right.$$
$$+ P_0[V_{A2}(t) - V_{A1}] - P_0[(V_0)_{A2}(t) - (V_0)_{A1}] \right\}$$
$$- T_0 \left\{ [S_{A2}(t) - S_{A1}] - [(S_0)_{A2}(t) - (S_0)_{A1}] \right\}$$

$$= \sum_i \left\{ \int_0^t \sum_k [(\overline{\beta}(t) - T_0\overline{\gamma}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] \, dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(\overline{\beta}(t) - T_0\overline{\gamma}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] \, dt \right\}_e$$

$$- \sum_{\ell} \left\{ \int_0^t \sum_k \left[(\bar{\beta}(t) - T_0 \bar{\gamma}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t) \right] dt \right\}_\ell$$

$$+ \int_0^t \left[|W_1(t)| - |W_2(t)| \right] dt - \int_0^t \left[|(W_x)_0(t)| + (T_0 \sigma(t)) \right] dt \tag{A-27}$$

By introducing the partial molar exergy defined as

$$\bar{\varepsilon} \equiv (\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0)$$

$$= \bar{\beta} - T_0 \bar{\gamma} , \tag{A-28}$$

we have

$$\left\{ [E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)] \right.$$
$$- [(E_0)_{A2}(t) + P_0 (V_0)_{A2}(t) - T_0 (S_0)_{A2}(t)] \right\}$$
$$- \left\{ [E_{A1} + P_0 V_{A1} - T_0 S_{A1}] - [(E_0)_{A1} + P_0 (V_0)_{A1} - T_0 (S_0)_{A1}] \right\}$$

$$= \sum_i \left\{ \int_0^t \sum_k \left[(\bar{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t) \right] dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k \left[(\bar{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t) \right] dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k \left[(\bar{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t) \right] dt \right\}_\ell$$

$$+ \int_0^t \left[|Q_1(t)| (1 - \frac{T_0}{T_{m1}}) - |Q_2(t)| (1 - \frac{T_0}{T_{m2}}) + |W_1(t)| - |W_2(t)| \right] dt$$

$$- \int_0^t \left[|(W_x)_0(t)| + (T_0 \sigma(t)) \right] dt \tag{A-29}$$

This is the expression of the available energy balance around an unsteady-state open flow system.

The concept of available energy, essergy, A_{es}, is defined as (see, e.g., Evans, 1969, 1980)

$$A_{es} \equiv (E + P_0 V - T_0 S) - \sum_k m_k (\bar{\mu}_0)_k \tag{A-30}$$

where $(\bar{\mu}_0)_k$ is the chemical potential of substance k at the dead state

and m_k the number of moles of substance k. Thus, we have

$$A_{es} = (E + P_0 V - T_0 S) - G_0$$

$$= (E + P_0 V - T_0 S) - (E_0 + P_0 V_0 - T_0 S_0) \qquad (A-31)$$

Comparing this expression with equation (A-29), it can be stated that

the left hand side of equation (A-29) is the change in essergy of system

A between state 1 and state 2.

NOMENCLATURE

0	= subscript representing the dead state
0	= superscript representing the standard state
A	= system A
a	= unit area of the control surface, m^2
A_{es}	= essergy, J
E	= total internal energy, J
e	= output streams
gx	= specific potential energy, J/kmol
$\overline{h}$	= partial molar enthalpy, J/kmol
i	= input streams
j	= molar flux, kmol/sec · m^2
k	= material species
ℓ	= leakage
M	= mass, kg
Mw	= molecular weight, kg/kmol
n	= molar flow rate including both convective and diffusional flows, kmol/sec
P	= pressure, atm
$|Q_0|$	= heat loss to the surroundings per unit time, J/sec
$|Q_1|$	= heat transferred from system M1 to system A per unit time, J/sec
$|Q_2|$	= heat transferred from system A to system M2 per unit time, J/sec
S	= entropy, J/K
$\overline{s}$	= partial molar entropy, J/K · kmol
T	= temperature, K
T_{m1}	= temperature of system M1, K

T_{m2} = temperature of system M2, K

t = time, sec

$u^2/2$ = specific kinetic energy, J/kmol

V = volume, m^3

$|W_0|$ = work lost to the surroundings per unit time, J/sec

$|W_1|$ = work supplied from system N1 to system A per unit time, J/sec

$|W_2|$ = work supplied from system A to system N2 per unit time, J/sec

$|W_{elec}|$ = electric work per unit time, J/sec

$|W_{mag}|$ = magnetic work per unit time, J/sec

$|W_P|$ = perpendicular work per unit time, J/sec

$|(W_P)_0|$ = work loss due to expansion of the boundary of the sytem per unit time, J/sec

$|W_t|$ = tangential work per unit time, J/sec

$|(W_x)_0|$ = work lost to the surroundings except that due to expansion of the boundary of system A per unit time, J/sec

GREEK

$\bar{\beta}$ = partial molar enthalpy relative to the dead state, J/kmol

$\bar{\beta}^0$ = parital molar chemical enthalpy, J/kmol

$\bar{\gamma}$ = partial molar entropy relative to the dead state, J/K · kmol

$\bar{\gamma}^0$ = partial molar chemical entropy, J/K · kmol

$\bar{\varepsilon}$ = partial molar exergy, J/kmol

$\bar{\varepsilon}^0$ = partial molar chemical exergy, J/kmol

σ = created entropy per unit time, J/K · sec

Ω = control surface

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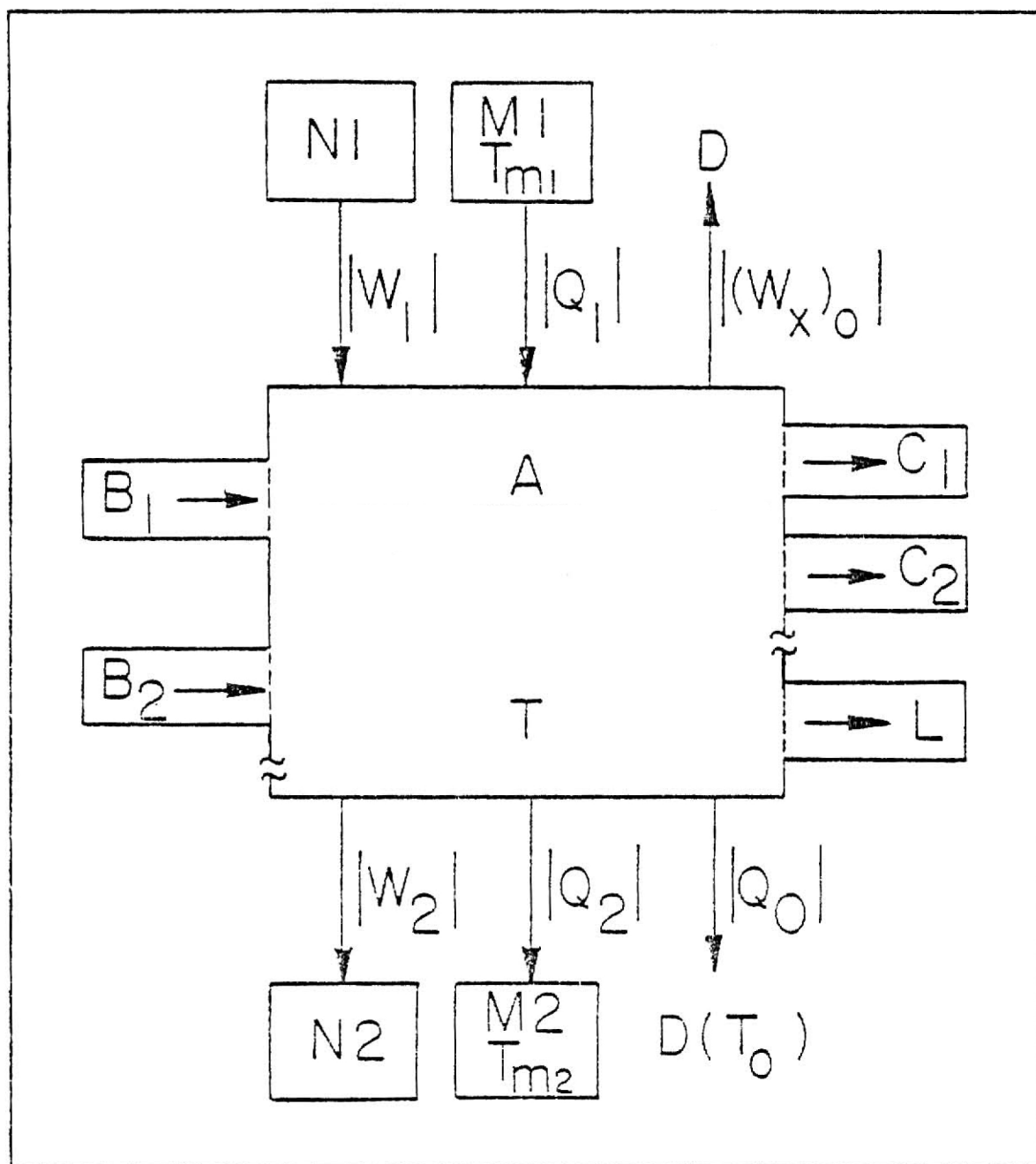
Fig. A-1. Schematic diagram of an open flow system.

APPENDIX B. DERIVATION OF THE EXPRESSIONS FOR

CALCULATING $\bar{\beta}$, $\bar{\gamma}$ AND $\bar{\epsilon}$

Formulas for evaluating the partial molar enthalpy relative to the
dead state, $\bar{\beta}$, the partial molar entropy relative to the dead state, $\bar{\gamma}$,
and the partial molar exergy, $\bar{\epsilon}$, are derived. For this purpose, 1 mol
of the constant-composition mixture is taken as a closed system. For
this system, the first law of thermodynamics is, conventionally,
expressed in differential form as

$$du = \delta Q - \delta W \tag{B-1}$$

where u is the molar internal energy, Q the heat transferred to the
system, W the work done by the system; symbol d stands for infinitesimal
changes of state properties and symbol δ for infinitesimal changes of
path variables.

Suppose that the process is reversible; then, equation (B-1) can be
rewritten as

$$du = \delta Q_{rev} - \delta W_{rev} \tag{B-2}$$

If it is assumed that the system is capable of performing the work only
through a change in volume of the system, we have

$$\delta W_{rev} = Pdv \tag{B-3}$$

wehre P is the pressure of the system and v the molar volume. Applying
the second law of thermodynamics to this reversible process, we have

$$\delta Q_{rev} = Tds \tag{B-4}$$

where T denotes the temperature of the system and s the molar entropy.
Combining equations (B-2) through (B-4), we have

$$du = Tds - Pdv \tag{B-5}$$

Note that this equation contains only the state properties of the

mixture and is independent of the path of the process; thus, it is valid not only for reversible processes, but also for irreversible processes. For the constant-composition mixture under consideration, we have the same expression as equation (B-5) for the corresponding partial molar properties of any component or material species in the mixture. Therefore, we can write

$$d\bar{u} = Td\bar{s} - Pd\bar{v} \qquad (B-6)$$

The molar enthalpy and partial molar enthalpy are defined, respectively, as

$$h = u + Pv \qquad (B-7)$$

$$\bar{h} = \bar{u} + P\bar{v} \qquad (B-8)$$

Thus, the differential of $\bar{h}$ is

$$d\bar{h} = d\bar{u} + Pd\bar{v} + \bar{v}dP$$

Substitution of equation (B-6) into this expression for $d\bar{u}$ yields

$$d\bar{h} = Td\bar{s} + \bar{v}dP \qquad (B-9)$$

The partial molar entropy, $\bar{s}$, may be expressed as a function of temperature and pressure. Thus,

$$\bar{s} = \bar{s}(T,P)$$

or, in differential form,

$$d\bar{s} = \left(\frac{\partial \bar{s}}{\partial T}\right)_P dT + \left(\frac{\partial \bar{s}}{\partial P}\right)_T dP \qquad (B-10)$$

For expanding the above equation, the specific heat at constant pressure, c_P, and the partial molar Gibbs free energy, $\bar{g}$, need be considered. The specific heat of any component of the mixture at constant pressure, $\bar{c}_P$, is defined as

$$\bar{c}_P \equiv \left(\frac{\partial \bar{h}}{\partial T}\right)_P \qquad (B-11)$$

Dividing equation (B-9) by dT, we have, under restriction of constant

pressure,

$$\left(\frac{\partial \bar{h}}{\partial T}\right)_P = T\left(\frac{\partial \bar{s}}{\partial T}\right)_P \tag{B-12}$$

Combination of this equation with equation (B-10) yields

$$\left(\frac{\partial \bar{s}}{\partial T}\right)_P = \frac{\bar{c}_P}{T} \tag{B-13}$$

The partial molar Gibbs free energy, $\bar{g}$, may be expressed as function of temperature and pressure, and thus,

$$\bar{g} = \bar{g}(T,P)$$

or, in differential form

$$d\bar{g} = \left(\frac{\partial \bar{g}}{\partial P}\right)_T dP + \left(\frac{\partial \bar{g}}{\partial T}\right)_P dT \tag{B-14}$$

Since

$$\bar{g} = \bar{h} - T\bar{s} , \tag{B-15}$$

the differential of $\bar{g}$ is

$$d\bar{g} = d\bar{h} - Td\bar{s} - \bar{s}dT \tag{B-16}$$

From equation (B-9), this equation becomes

$$d\bar{g} = \bar{v}dP - \bar{s}dT \tag{B-17}$$

Comparison of this equation with equation (B-14) gives

$$\bar{v} = \left(\frac{\partial \bar{g}}{\partial P}\right)_T \tag{B-18}$$

and

$$-\bar{s} = \left(\frac{\partial \bar{g}}{\partial T}\right)_P \tag{B-19}$$

Further differentiation of these two expressions gives, respectively,

$$\left(\frac{\partial \bar{v}}{\partial T}\right)_P = \frac{\partial^2 \bar{g}}{\partial P \partial T} \tag{B-20}$$

and

$$-\left(\frac{\partial \bar{s}}{\partial P}\right)_T = \frac{\partial^2 \bar{g}}{\partial T \partial P} \tag{B-21}$$

Therefore, we have

$$\left(\frac{\partial \bar{v}}{\partial T}\right)_P = -\left(\frac{\partial \bar{s}}{\partial P}\right)_T \tag{B-22}$$

This is one of the Maxwell relations.

Substituting equation (B-13) and (B-22) into equation (B-10), we

have

$$d\bar{s} = \frac{\bar{c}_P}{T} \, dT - \left(\frac{\partial \bar{v}}{\partial T}\right)_P \, dP \qquad (B-23)$$

Substituting this expression into (B-9), we have

$$d\bar{h} = \bar{c}_P \, dT + [\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P] \, dP \qquad (B-24)$$

The partial molar enthalpy relative to the dead state, $\bar{\beta}$, is

defined as

$$\bar{\beta} \equiv \bar{h} - \bar{h}_0 \qquad (B-25)$$

where subscript 0 stands for the dead state; letting superscript 0

denote the standard state, we have

$$\bar{\beta} = (\bar{h} - \bar{h}^0) + (\bar{h}^0 - \bar{h}_0)$$
$$= \bar{\beta}^0 + (\bar{h} - \bar{h}^0) \qquad (B-26)$$

where

$$\bar{\beta}^0 \equiv \bar{h}^0 - \bar{h}_0 \qquad (B-27)$$

Substituting equation (B-24) into equation (B-26), we have

$$\bar{\beta} = \bar{\beta}^0 + \int_{T^0}^{T} \bar{c}_P \, dT + \int_{P^0}^{P} [\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_P] \, dP \qquad (B-28)$$

where the first, second and third terms in the right-hand side may be

named, respectively, the partial molar chemical enthalpy, partial molar

thermal enthalpy and partial molar pressure enthalpy.

For obtaining a formula to estimate the partial molar chemical

enthalpy, $\bar{\beta}^0$, we consider a steady-state open flow system, system A,

shown in Fig. B-1, which carries out a chemical reaction. It is assumed

that no heat loss or material leakage to the surroundings exists and

only the thermal form of energy is transmitted between system A and a

heat source or sink. Provided that system A is under the condition of

the standard state, we have, at the inlet and the outlet of system A,

$$T = T^0 = 298.15 \text{ K}$$

$$P = P^0 = 1 \text{ atm}$$

and

$$x_k = x_k^0 = 1$$

where x_k is the mole fraction of material species k.

According to the stoichiometry of the chemical reaction under consideration, the energy balance around system A can be expressed as

$$\sum_i (\sum_k \bar{\beta}_k^0 \nu_k)_i + Q = \sum_e (\sum_k \bar{\beta}_k^0 \nu_k)_e \qquad (B-29)$$

where ν_k is the stoichiometric coefficient of substance k, and Q the heat transferred between system A and the heat source or sink. Conventionally, Q is regarded as positive when it is transferred into system A and as negative when it is transferred out of it. It should be noted that, in equation (B-29), Q is specified in such a way that it is transferred in the time period during which $\nu_{k,i}$ moles of reactant k(k=1,2,...,r) enter system A and $\nu_{k,e}$ moles of product k(k=1,2,...,p) exit from system A. Also note that

$$Q = \Delta H_r^0 \qquad (B-30)$$

because ΔH_r^0 is the heat reaction at the standard state and it is positive if the reaction is endothermic, and negative if it is exothermic. Therefore, equation (B-29) can be rewritten as

$$\sum_i (\sum_k \bar{\beta}_k^0 \nu_k)_i + \Delta H_r^0 = \sum_e (\sum_k \bar{\beta}_k^0 \nu_k)_e \qquad (B-31)$$

Equations (B-28) and (B-31) are the working formulas for determining the enthalpy relative to the dead state.

The partial molar entropy relative to the dead state, $\bar{\gamma}$, is defined as

$$\bar{\gamma} \equiv \bar{s} - \bar{s}_0 , \qquad (B-32)$$

and thus, it can be written as

$$\bar{\gamma} = (\bar{s} - \bar{s}^0) + (\bar{s}^0 - \bar{s}_0)$$
$$= \bar{\gamma}^0 + (\bar{s} - \bar{s}^0) \tag{B-33}$$

where

$$\bar{\gamma}^0 \equiv \bar{s}^0 - \bar{s}_0 \tag{B-34}$$

Substitution of equation (B-23) into equation (B-33) yields

$$\bar{\gamma} = \bar{\gamma}^0 + \int_{T^0}^{T} \frac{\bar{c}_P}{T} \, dT - \int_{P^0}^{P} \left(\frac{\partial v}{\partial T}\right)_P \, dP \tag{B-35}$$

where the first, second and third terms of the right-hand side may be termed, respectively, the partial molar chemical entropy, partial molar thermal entropy and partial molar pressure entropy.

To obtain a formula for estimating the partial molar chemical entropy, $\bar{\gamma}^0$, the entire system shown in Fig. B-1 is considered. The entropy balance around system A can be expressed as

$$\sigma = -\sum_i (\sum_k \bar{\gamma}_k^0 \nu_k)_i + \sum_e (\sum_k \bar{\gamma}_k^0 \nu_k)_e - \frac{Q}{T_m} \tag{B-36}$$

where σ denotes the created entropy and T_m the temperature of the heat source or sink. Rearrangement of equation (B-36) gives

$$\sum_i (\sum_k \bar{\gamma}_k^0 \nu_k)_i + (\frac{Q}{T_m} + \sigma) = \sum_e (\sum_k \bar{\gamma}_k^0 \nu_k)_e \tag{B-37}$$

The entropy change of reaction at the standard state, Δs_r^0, is defined as the difference between the entropy of the products and that of the reactants when they are all at the standard state. Thus, by definition, Δs_r^0 corresponds to the second term in the left-hand side of equation (B-37), i.e.,

$$(\frac{Q}{T_m} + \sigma) = \Delta s_r^0 \tag{B-38}$$

Therefore, equation (B-37) can be rewritten as

$$\sum_i \left(\sum_k \bar{\gamma}_k^0 \, \nu_k \right)_i + \Delta S_r^0 = \sum_e \left(\sum_k \bar{\gamma}_k^0 \, \nu_k \right)_e \qquad \text{(B-39)}$$

Equations (B-35) and (B-39) are the working formulas for determining the entropy relative to the dead state.

The partial molar exergy, $\bar{\varepsilon}$, is defined as

$$\bar{\varepsilon} \equiv (\bar{h} - \bar{h}_0) - T_0(\bar{s} - \bar{s}_0)$$

$$= \bar{\beta} - T_0 \, \bar{\gamma} \quad , \qquad \text{(B-40)}$$

and thus, substituting equations (B-28) and (B-35), we have

$$\varepsilon = (\bar{\beta}^0 - T_0 \, \bar{\gamma}^0) + \int_{T^0}^{T} \bar{c}_p \left(1 - \frac{T_0}{T}\right) dT$$

$$+ \int_{P^0}^{P} \left[\bar{v} - (T - T_0)\left(\frac{\partial \bar{v}}{\partial T}\right)_P \right] dP \qquad \text{(B-41)}$$

By defining

$$\bar{\varepsilon}^0 \equiv \bar{\beta}^0 - T_0 \, \bar{\gamma}^0 \quad , \qquad \text{(B-42)}$$

we have

$$\bar{\varepsilon} = \bar{\varepsilon}^0 + \int_{T^0}^{T} \bar{c}_p \left(1 - \frac{T_0}{T}\right) dT$$

$$+ \int_{P^0}^{P} \left[\bar{v} - (T - T_0)\left(\frac{\partial v}{\partial T}\right)_P \right] dP \qquad \text{(B-43)}$$

where the first, second and third terms of the right-hand side of this equation may be named, respectively, the partial molar chemical exergy, partial molar thermal exergy and partial molar pressure exergy.

Subtracting equation (B-39) multiplied by T_0 from equation (B-31), we have

$$\sum_i \left(\sum_k \bar{\varepsilon}_k^0 \, n_k \right)_i + \Delta G_r^0 = \sum_e \left(\sum_k \bar{\varepsilon}_k^0 \, n_k \right)_k \qquad \text{(B-45)}$$

where ΔG_r^0 is the Gibbs free energy change of reaction at the standard state. Equations (B-43) and (B-45) are the working formulas to determining the exergy.

NOMENCLATURE

0	= subscript representing the dead state
0	= superscript representing the standard state
$\bar{c}_P$	= specific heat, J/kmol $\cdot$ K
e	= output streams
ΔG_r^0	= Gibbs free energy change of reaction at the standard state, J
$\bar{g}$	= partial molar Gibbs free energy, J/kmol
ΔH_r^0	= heat of reaction at the standard state, J
h	= molar enthalpy, J/kmol
$\bar{h}$	= partial molar enthalpy, J/kmol
i	= input streams
k	= material species
P	= pressure, atm
Q	= heat, J
ΔS_r^0	= entropy change of reaction at the dead state, J/k
s	= molar entropy, J/K $\cdot$ kmol
$\bar{s}$	= partial molar entropy, J/K $\cdot$ kmol
T	= temperature, K
T_m	= temperature of heat source or sink, K
u	= molar internal energy, J/kmol
$\bar{u}$	= partial molar internal energy, J/kmol
v	= molar volume, m^3/kmol
$\bar{v}$	= partial molar volume, m^3/kmol
W	= work, J
x_k	= mole fraction of substance k

GREEK

$\overline{\beta}$ = partial molar enthalpy relative to the dead state, J/kmol

$\overline{\beta}^0$ = partial molar chemical enthalpy, J/kmol

$\overline{\gamma}$ = partial molar entropy relative to the dead state, J/K · kmol

$\overline{\gamma}^0$ = partial molar chemical entropy, J/K · kmol

$\overline{\epsilon}$ = partial molar exergy, J/kmol

$\overline{\epsilon}^0$ = partial molar chemical exergy, J/kmol

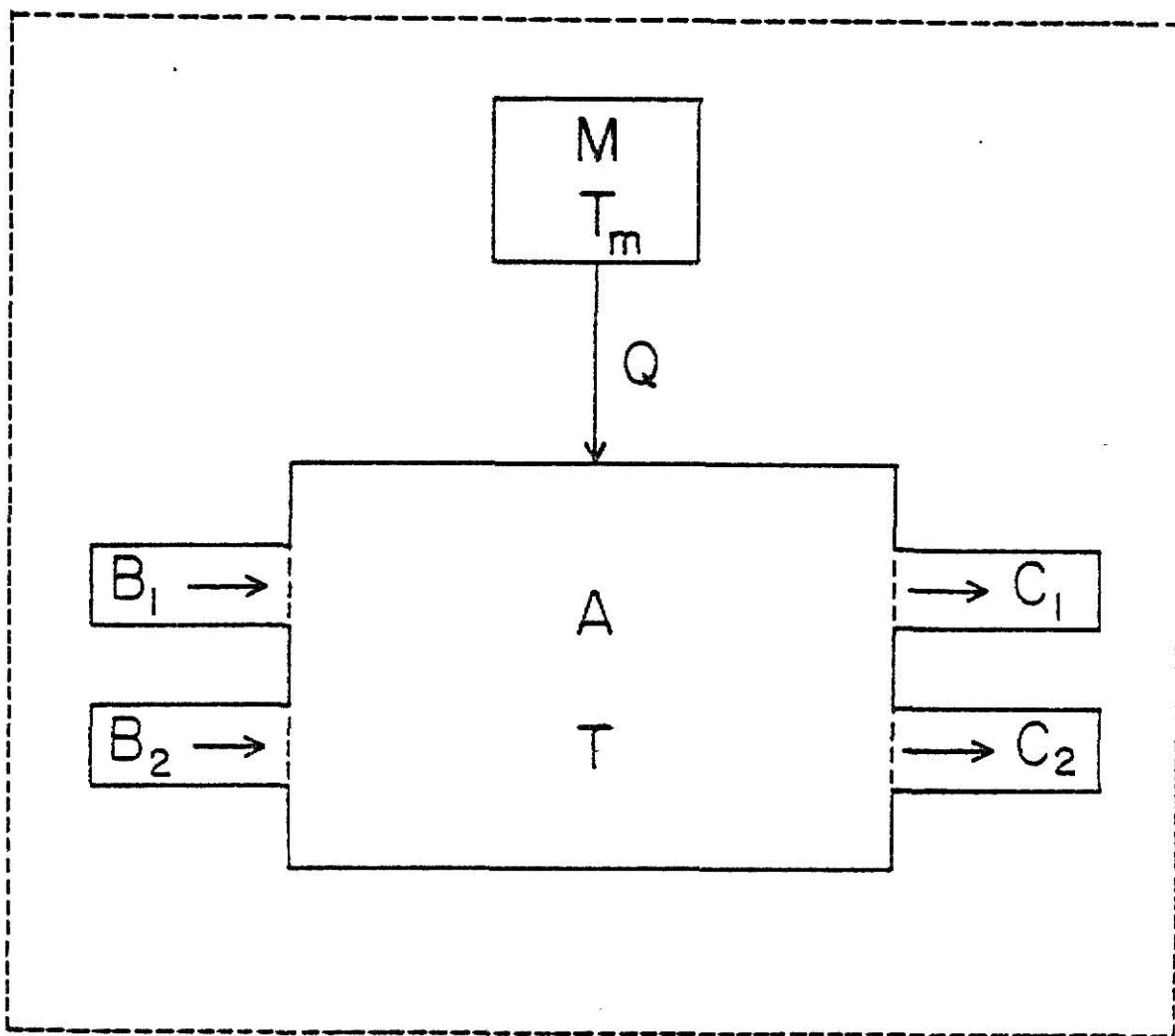σ = created entropy per unit time, J/K · sec

Fig. B-1. Schematic diagram of a steady-state open flow system.

APPENDIX C.   VARIOUS EXPRESSIONS OF THE AVAILABLE ENERGY

The available energy balance for an unsteady-state open flow system gives rise to the definitions of exergy and essergy, as shown in chapter 3 and appendix A; the exergy is often expressed in terms of the Gibbs free energy, chemical potential and availability function. In this appendix, various expressions and forms of the exergy are presented, and the relationship between exergy and essergy is derived (see, e.g., Keenan, 1941; Rant, 1956; Denbigh, 1956, 1971; Gaggioli, 1961, 1980; Szargut and Petela, 1965; Evans, 1969; Riekert, 1974; Haywood, 1974, 1980; Gaggioli and Petit, 1977; Fan and Shieh, 1980).

Selecting the temperature, T, the pressure, P, and the number of moles of each substance or material species, m_k, as independent variables, any thermodynamic property, A, of a given mixture can be expressed as

$$A = A(T, P, m_1, m_2, \ldots, m_{n-1})$$

where n is the total number of components or material species in the mixture. By definition, the partial molar property of component k in the mixture, $\bar{a}_k$, is

$$\bar{a}_k = \left(\frac{\partial A}{\partial m_k}\right)_{T,P,m_j} \tag{C-1}$$

where subscript m_j indicates that all mole numbers except that of the k-th component are held constant. The lower case with an overbar identifies it as a partial molar property. Since the property, A, is homogeneous of degree one in the mole numbers, we have

$$\alpha A (T, P, m_1, m_2, \ldots, m_{n-1})$$
$$= A (T, P, \alpha m_1, \alpha m_2, \ldots, \alpha m_{n-1})$$

Thus,

$$A = \sum_k m_k \bar{a}_k \qquad (C-2)$$

Furthermore, the molar property of the mixture, a, is defined as

$$a = \frac{A}{m} \quad \text{or} \quad A = ma \qquad (C-3)$$

where

$$m = \sum_k m_k \qquad (C-4)$$

Equating equation (C-3) to equation (C-2), we have

$$ma = \sum_k m_k \bar{a}_k \qquad (C-5)$$

Dividing both sides of this expression by m yields

$$a = \sum_k x_k \bar{a}_k \qquad (C-6)$$

where x_k is the mole fraction of component k in the mixture defined as

$$x_k = \frac{m_k}{m} \qquad (C-7)$$

The partial molar exergy of an arbitrary component in the mixture, $\bar{\varepsilon}$, is defined as (see, e.g., Fan and Shieh, 1980)

$$\bar{\varepsilon} \equiv (\bar{h}-\bar{h}_0) - T_0(\bar{s}-\bar{s}_0) \qquad (C-8)$$

where $\bar{h}$ stands for the partial molar enthalpy, $\bar{s}$ for the partial molar entropy, and subscript 0 denotes the dead state, where the system is at rest relative to the environment and is equilibrium with it with respect to pressure, temperature, electricity, magnetism and composition. From this expression, we have

$$\bar{\varepsilon} = (\bar{h}-T_0\bar{s}) - (\bar{h}_0-T_0\bar{s}_0)$$
$$= (\bar{h}-T_0\bar{s}) - \bar{g}_0 \qquad (C-9)$$

or

$$\bar{\varepsilon} = (\bar{h}-T_0\bar{s}) - \mu_0 \qquad (C-10)$$

where $\bar{g}_0$ is the partial molar Gibbs free energy at the dead state, μ_0

the chemical potential at the dead state. Note that

$$\mu_0 = \bar{g}_0$$
$$= \bar{h}_0 - T_0\bar{s}_0$$

Equations (C-9) and (C-10) are the alternative forms for expressing the partial molar exergy defined by equation (C-8).

By resorting to equation (C-6), the molar exergy, ε, of mixture is expressed as

$$\varepsilon = \sum x_k \bar{\varepsilon}_k \qquad (C-11)$$

and thus, on the basis of a unit mole of the mixture,

$$\varepsilon = \sum_k x_k (\bar{h}_k - T_0\bar{s}_0) - \sum_k x_k [(\bar{h}_0)_k - T_0(\bar{s}_0)_k]$$

$$= (h - T_0 s) - (h_0 - T_0 s_0)$$

$$= (h - T_0 s) - g_0 \qquad (C-12)$$

or

$$\varepsilon = (h - T_0 s) - \sum_k x_k (\mu_0)_k \qquad (C-13)$$

where h, s and g denote, respectively, the molar enthalpy, entropy and Gibbs free energy of the mixture. Furthermore, by defining the availability function, b, as (see, e.g., Keenan, 1941)

$$b \equiv h - T_0 s \quad , \qquad (C-14)$$

we have, on the basis of a unit mole of the mixture,

$$\varepsilon = b - b_0 \qquad (C-15)$$

Equations (C-12), (C-13) and (C-15) are the alternative forms to express the molar exergy.

Additionally, the partial molar chemical exergy, $\bar{\varepsilon}^0$, is defined as

$$\bar{\varepsilon}^0 \equiv (\bar{h}^0 - \bar{h}_0) - T_0(\bar{s}^0 - \bar{s}_0) \qquad (C-16)$$

where superscript 0 denotes the standard state, where the system is equilibrium with the environment with regard to the temperature and pressure. Note that, usually,

$$T_0 = T^0 , \tag{C-17}$$

and thus, equation (C-6) can be rewritten as

$$\bar{\varepsilon}^0 = (\bar{h}^0 - T^0 \bar{s}^0) - (\bar{h}_0 - T_0 \bar{s}_0)$$

$$= \bar{g}^0 - \bar{g}_0 \tag{C-18}$$

or

$$\bar{\varepsilon}^0 = \mu^0 - \mu_0 \tag{C-19}$$

By resorting to equation (C-6), on the basis of a unit mole of the mixture, we have

$$\varepsilon^0 = \sum_k x_k [(\mu^0)_k - (\mu_0)_k] \tag{C-20}$$

The essergy is defined as (see, e.g., Evans, 1969, 1980)

$$A_{es} \equiv E + P_0 V - T_0 S - \sum_k m_k (\mu_0)_k \tag{C-21}$$

or by resorting to equations (C-2) through (C-6), the molar essergy can be expressed as

$$a_{es} \equiv e + P_0 v - T_0 s - \sum_k x_k (\mu_0)_k \tag{C-22}$$

where E is the total internal energy including kinetic energy, potential energy, etc., and m_k the number of moles of substance k. The total internal energy, e, can be expressed as

$$e = u + gx + \frac{u^2}{2} + \ldots \tag{C-23}$$

where u is the molar internal energy, gx the molar potential energy and $\frac{u^2}{2}$ the molar kinetic energy; the dotted line in the right-hand side indicates that other forms of energy, such as the electric and magnetic energy, need be considered in general. Comparing equation (C-13) with equation (C-22), we have

$$\varepsilon = (u + Pv - T_0 s) - \sum_k x_k \, (\mu_0)_k$$

$$= [(u + gx + \frac{u^2}{2} + \ldots) + P_0 v - T_0 s] - \sum_k x_k \, (\mu_0)_k$$

$$- (gx + \frac{u^2}{2} + \ldots) - P_0 v + Pv$$

$$= (e + P_0 v - T_0 s) - \sum x_k \, (\mu_0)_k$$

$$+ (P-P_0)v - (gx + \frac{u^2}{2} + \ldots)$$

$$= a_{es} + (P-P_0)v - (gx + \frac{u^2}{2} + \ldots) \tag{C-24}$$

Furthermore, the partial molar essergy is expressed as

$$\bar{a}_{es} = \bar{e} + P_0 \bar{v} - T_0 \bar{s} - \bar{\mu}_0 \tag{C-25}$$

Therefore, comparison of this equation with equation (C-10) gives an expression similar to equation (C-24), i.e.,

$$\bar{\varepsilon} = \bar{a}_{es} + (P-P_0)\bar{v} - (gx + \frac{u^2}{2} + \ldots) \tag{C-26}$$

The essergy appears in the available energy balance for an unsteady-state open flow system, equation (A-28) in appendix A or equation (11) in Chapter 3.

NOMENCLATURE

0 = subscript denoting the dead state

0 = superscript denoting the standard state

A = thermodynamic property

A_{es} = essergy, J

a_{es} = molar essergy, J/kmol

$\bar{a}_{es}$ = partial molar essergy, J/kmol

$\bar{a}_k$ = partial molar property of component k

b = availability function, J/kmol

E = total internal energy, J

e = molar total internal energy, J/kmol

g = molar Gibbs free energy, J/kmol

$\bar{g}$ = partial molar Gibbs free energy, J/kmol

gx = specific potential energy, J/kmol

h = molar enthalpy, J/kmol

$\bar{h}$ = partial molar enthalpy, J/kmol

m_k = number of moles of substance k

s = molar entropy, J/K · kmol

$\bar{s}$ = partial molar entropy, J/K · kmol

$u^2/2$ = specific kinetic energy, J/kmol

u = molar internal energy, J/kmol

x_k = mole fraction of substance k

GREEK

β = molar enthalpy relative to the dead state, J/kmol

$\bar{\beta}$ = partial molar enthalpy relative to the dead state, J/kmol

$\bar{\beta}^0$ = partial molar chemical enthalpy, J/kmol

γ = molar entropy relative to the dead state, $J/K \cdot kmol$

$\bar{\gamma}$ = partial molar entropy relative to the dead state, $J/kmol \cdot K$

$\bar{\gamma}^0$ = partial molar chemical entropy, $J/kmol \cdot K$

ε = molar exergy, $J/kmol$

$\bar{\varepsilon}$ = partial molar exergy, $J/kmol$

$\bar{\varepsilon}^0$ = partial molar chemical exergy, J/mol

μ = chemical potential, $J/kmol$

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APPENDIX D.   SPECIAL CASE OF THE AVAILABLE ENERGY ANALYSIS--
THE SO-CALLED LOST WORK ANALYSIS

The expression of the available energy balance may be rearranged for some special purposes (see, e.g., Keenan, 1932). For convenience, the same overall system, shown in Fig. A-1, is considered.

The available energy balance for an unsteady-state open flow system, derived in Appendix A, equation (A-29), is

$$
\{[E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)]
$$

$$
- [(E_0)_{A2}(t) + P_0(V_0)_{A2}(t) - T_0(S_0)_{A2}(t)]\}
$$

$$
- \{[E_{A1} + P_0 V_{A1} - T_0 S_{A1}] - [(E_0)_{A1} + P_0(V_0)_{A1} - T_0(S_0)_{A1}]\}
$$

$$
= \sum_i \left\{ \int_0^t \sum_k [(\overline{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_i
$$

$$
- \sum_e \left\{ \int_0^t \sum_k [(\overline{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_e
$$

$$
- \sum_\ell \left\{ \int_0^t \sum_k [(\overline{\varepsilon}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_\ell
$$

$$
+ \int_0^t [|Q_1(t)| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2(t)| \, (1 - \frac{T_0}{T_{m2}}) + |W_1(t)| - |W_2(t)|] dt
$$

$$
- \int_0^t [|(W_x)_0(t)| + (T_0 \sigma(t))] dt \tag{D-1}
$$

where

$$
\overline{\varepsilon} = (\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) \tag{D-2}
$$

On the other hand, combination of the energy balance equation (A-14), and the entropy balance, equation (A-23), for system A at the dead state gives rise to

$$[(E_0)_{A2}(t) + P_0(V_0)_{A2}(t) - T_0(S_0)_{A2}(t)]$$

$$- [(E_0)_{A1} + P_0(V_0)_{A1} - T_0(S_0)_{A1}]$$

$$= \sum_i \left\{ \int_0^t \sum_k [\overline{h}_0(t) - T_0\overline{s}_0(t)]_k \, n_k(t) \, dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [\overline{h}_0(t) - T_0\overline{s}_0]_k \, n_k(t) \, dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [\overline{h}_0(t) - T_0\overline{s}_0]_k \, n_k(t) \, dt \right\}_\ell \qquad (D-3)$$

Note that

$$\overline{\varepsilon} + (\overline{h}_0 - T_0\overline{s})$$

$$= (\overline{h} - \overline{h}_0) - T_0(\overline{s} - \overline{s}_0) + (\overline{h}_0 - T_0\overline{s}_0)$$

$$= \overline{h} - T_0\overline{s}$$

$$= \overline{b}$$

where $\overline{b}$ is the partial molar availability function; thus, adding each side of equation (D-1) to the corresponding side of equation (D-3), we have

$$[E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)]$$

$$- [E_{A1} + P_0 V_{A1} - T_0 S_{A1}]$$

$$= \sum_i \left\{ \int_0^t \sum_k [(\overline{b}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(\overline{b}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(\overline{b}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)] dt \right\}_\ell$$

$$+ \int_0^t [|Q_1(t)| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2(t)| \, (1 - \frac{T_0}{T_{m2}})] \, dt$$

$$+ \int_0^t [|W_1(t)| - |W_2(t)|]dt$$

$$- \int_0^t [|(W_x)_0(t)| + (T_0\sigma(t))]dt \qquad (D-4)$$

The last term of the right-hand side of this equation

$$\int_0^t [|(W_x)_0(t)| + (T_0\sigma(t))]dt$$

represents the available energy dissipation, which may be called irreversibility (see, e.g., Keenan, 1941; Fan and Shieh, 1980). This expression can also be obtained directly by combining the energy balance, equation (A-11), with the entropy balance, equation (A-22). Rearrangement of equation (D-4) yields

$$\int_0^t [|W_2(t)| - |W_1(t)| + |(W_x)_0(t)| + (T_0\sigma(t))]dt$$

$$= \sum_i \left\{ \int_0^t \sum_k [(\overline{b}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)]dt \right\}_i$$

$$- \sum_e \left\{ \int_0^t \sum_k [(\overline{b}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)]dt \right\}_e$$

$$- \sum_\ell \left\{ \int_0^t \sum_k [(\overline{b}(t) + gx(t) + \frac{u(t)^2}{2} + \ldots)_k \, n_k(t)]dt \right\}_\ell$$

$$+ \int_0^t [|Q_1(t)| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2(t)| \, (1 - \frac{T_0}{T_{m2}})] \, dt$$

$$- \left\{ [E_{A2}(t) + P_0 V_{A2}(t) - T_0 S_{A2}(t)] - [E_{A1} + P_0 V_{A1} - T_0 S_{A1}] \right\} \qquad (D-5)$$

In this expression, the left-hand side represents the net reversible work of this system.

For a steady-state open flow system having negligible kinetic energy, potential energy, etc., equation (D-5) reduces to

$$[|W_2| - |W_1| + |(W_x)_0| + (T_0\sigma)]$$

$$= \sum_i (\sum_k \overline{b}_k \, n_k)_i - \sum_e (\sum_k \overline{b}_k \, n_k)_e - \sum_\ell (\sum_k \overline{b}_k \, n_k)_\ell$$

$$+ |Q_1| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2| \, (1 - \frac{T_0}{T_{m2}}) \qquad \text{(D-6)}$$

Letting $|W_{n,r}|$ denote the net reversible work, we have

$$|W_{n,r}| = [\sum_i (\sum_k \overline{b}_k \, n_k)_i - \sum_e (\sum_k \overline{b}_k \, n_k)_e - \sum_\ell (\sum_k b_k \, n_k)_\ell]$$

$$+ [|Q_1| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2| \, (1 - \frac{T_0}{T_{m2}})] \qquad \text{(D-7)}$$

or assuming that there is no leakage from the system, we have

$$|W_{n,r}| = [\sum_i (\sum_k \overline{b}_k \, n_k)_i - \sum_e (\sum_k \overline{b}_k \, n_k)_e]$$

$$+ [|Q_1| \, (1 - \frac{T_0}{T_{m1}}) - |Q_2| \, (1 - \frac{T_0}{T_{m2}})] \qquad \text{(D-8)}$$

This equation is identical to the expression obtained by the so-called lost work analysis (see, e.g., Nevers and Seader, 1980; Nevers, 1982).

The lost work analysis is based upon the comparison of actual work with reversible work; the difference is called lost work, which corresponds to the available energy dissipation or irreversibility. Note that the terms containing the availability functions, $\overline{b}$, in equations (D-4) through (D-8) do not represent the available energy contents of process streams. Accordingly, caution should be exercised in using the availability function for any purpose other than computation of a difference in the available energy contents (see, e.g., Keenan, 1941; Moran, 1982).

NOMENCLATURE

0	=	subscript denoting the dead state
0	=	superscript denoting the standard state
A	=	syste A
b	=	molar availability function, J/kmol
$\bar{b}$	=	partial molar availability function, J/kmol
E	=	total internal energy, J
e	=	output streams
gx	=	specific potential energy, J/kmol
$\bar{h}$	=	partial molar enthalpy, J/kmol
i	=	input streams
k	=	material species
ℓ	=	leakage
M	=	mass, kg
Mw	=	molecular weight, kg/kmol
n	=	molar flow rate including both convective and diffusional flows, kmol/sec
P	=	pressure, atm
$|Q_0|$	=	heat loss to the surroundings per unit time, J/sec
$|Q_1|$	=	heat transferred from system M1 to system A per unit time, J/sec
$|Q_2|$	=	heat transferred from system A to system M2 per unit time, J/sec
S	=	entropy, J/K
$\bar{s}$	=	partial molar entropy, J/K $\cdot$ kmol
T	=	temperature, K
T_{m1}	=	temperature of system M1, K
T_{m2}	=	temperature of system M2, K

t = time, sec

$u^2/2$ = specific kinetic energy, J/kmol

V = volume, m^3

$|W_0|$ = work lost to the surroundings per unit time, J/sec

$|W_1|$ = work supplied from system N1 to system A per unit time, J/sec

$|W_2|$ = work supplied from system A to system N2 per unit time, J/sec

$|W_{n,r}|$ = net reversible work per unit time, J/sec

$|(W_x)_0|$ = work lost to the surroundings except that due to expansion of the boundary of system A per unit time, J/sec

GREEK

$\overline{\epsilon}$ = partial molar exergy, J/kmol

σ = created entropy per unit time, J/K · sec

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APPENDIX E. MACROSCOPIC MASS, ENERGY, ENTROPY AND AVAILABLE
ENERGY BALANCES FOR AN UNSTEADY-STATE OPEN FLOW SYSTEM

The macroscopic mass, energy, entropy and available energy balances

for an unsteady-state open flow system, depicted in Fig. E-1, are

derived from the corresponding microscopic balances.

MASS BALANCE

The microscopic equation of continuity is written as (see, e.g.,

Bird et al., 1960; White, 1979; Boder and Kenyon, 1980)

$$\frac{\partial \rho}{\partial t} = -(\nabla \cdot \rho \, \vec{v}) \tag{E-1}$$

where ρ is the density of a small volume element and $\vec{v}$ the vector

representation of the fluid velocity. The integration of equation (E-1)

over the volume, V, gives

$$\iiint_V \frac{\partial \rho}{\partial t} \, dV = -\iiint_V (\nabla \cdot \rho \, \vec{v}) \, dV \tag{E-2}$$

Applying the Leibnitz formula and the Gauss-Ostrogradskii divergence

theorem, respectively, to the left-hand and right-hand sides, we have

$$\frac{d}{dt} \iiint_V \rho \, dV - \iint_A \rho \, v_{s,n} \, dA = -\iint_A \rho \, v_n \, dA \tag{E-3}$$

where v_s denotes the velocity of any surface element, dA, and subscript

n indicates the component of the vector normal to the surface.

Rearrangement of this equation yields

$$\frac{d}{dt} \iiint_V \rho \, dV = -\iint_A \rho [v_n - v_{s,n}] \, dA \tag{E-4}$$

Letting $\vec{v}_r$ be the relative velocity defined as

$$\vec{v}_r \equiv \vec{v} - \vec{v}_s \tag{E-5}$$

we have

$$\frac{d}{dt} \iiint_V \rho \, dV = -\iint_A \rho \, v_{r,n} \, dA \tag{E-6}$$

This is the macroscopic expression of the mass balance.

Applying equation (E-6) to the system shown in Fig. A-1, whose state is a function of time, t, we can write the left-hand side of the equation as

$$\frac{d}{dt} \iiint_V \rho \; dV = \frac{dM_A}{dt} \tag{E-7}$$

where M_A is the mass in system A. The right-hand side of equation (E-6) can be written as

$$\iint_A \rho \; v_{r,n} \; dA = - \left[\iint_A \sum_k (Mw)_k \; j_k(t,A) \; dA \right]_i$$

$$+ \left[\iint_A \sum_k (Mw)_k \; j_k(t,A) \; dA \right]_e$$

$$+ \left[\iint_A \sum_k (Mw)_k \; j_k(t,A) \; dA \right]_\ell \tag{E-8}$$

or

$$\iint_A \rho \; v_{r,n} \; dA = - \sum_i \left[\sum_k (Mw)_k \; n_k(t) \right]_\ell$$

$$+ \sum_e \left[\sum_k (Mw)_k \; n_k(t) \right]_e$$

$$+ \sum_\ell \left[\sum_k (Mw)_k \; n_k(t) \right]_\ell \tag{E-8a}$$

where Mw the molecular weight, j the molar flux and n the molar flow rate including both the convetive and diffusional flows; furthermore, in equations (E-8) and (E-8a), subscript k stands for the k-th material species, i the inlet streams, e the outlet streams and ℓ the leakage streams. The direction of the outward normal at the inlet surface is opposite to that of the velocity vector on that surface; note that the minus sign appears with the input streams and the plus sign with the output streams. Equating equation (E-7) to equations (E-8) and (E-8a), we have, respectively,

$$\frac{dM_A}{dt} = [\iint_A \sum_k (Mw)_k \ j_k(t,A) \ dA]_i - [\iint_A \sum_k (Mw)_k \ j_k(t,A) \ dA]_e$$

$$-[\iint_A \sum_k (Mw)_k \ j_k(t,A) \ dA]_\ell \qquad (E-9)$$

and

$$\frac{dM_A}{dt} = \sum_i [\sum_k (Mw)_k \ n_k(t)]_i - \sum_e [\sum_k (Mw)_k \ n_k(t)]_e$$

$$- \sum_\ell [\sum_k (Mw)_k \ n_k(t)]_\ell \qquad (E-10)$$

The integration of equation (E-9) over the time interval, ranging from 0 to t, yields the expression corresponding to equation (A-2); the integration of equation (E-10) gives the expression corresponding to equation (A-4) in appendix A or equation (1) in Chapter 3.

ENERGY BALANCE

The microscopic energy balance around system A yields the expression for the energy balance as (see, e.g., Bird et al., 1960; White, 1979; Boder and Kenyon, 1980)

$$\frac{\partial}{\partial t} \rho \hat{e} = -(\nabla \cdot \rho \hat{e} \vec{v}) - (\nabla \cdot \vec{w}) - (\nabla \cdot \vec{q}) \qquad (E-11)$$

where $\hat{e}$ is the total internal energy per unit mass, $\vec{v}$ the fluid velocity, and $\vec{w}$ and $\vec{q}$, respectively, the work flux and heat flux between the differential volume element, dV, and the surroundings or any one of other systems through the elementary area, dA; the left-hand side of this equation represents the rate of the energy accumulation per unit volume, and the first, second and third terms of the right-hand side represent, respectively, the rate of the net energy input per unit volume associated with the material flow, the rate of the net work input per unit volume and the rate of the net heat input per unit volume.

Note that $\vec{w}$ is a collection of all forms of work. The integration of equation (E-11) over the volume of the system under consideration, V, gives rise to

$$\iiint_V \frac{\partial}{\partial t} (\rho \hat{e}) \, dV = -\iiint_V (\nabla \cdot \rho \hat{e} \vec{v}) \, dV$$

$$- \iiint_V (\nabla \cdot \vec{w}) \, dV - \iiint_V (\nabla \cdot \vec{q}) \, dV \quad \text{(E-12)}$$

By transforming the left-hand side and the right-hand side by means of the Leibnitz formula and the Gauss-Ostrogradskii divergence theorem, respectively, equation (E-12) becomes

$$\frac{d}{dt} \iiint_V \rho \hat{e} \, dV - \iint_A \rho \hat{e} \, v_{s,n} \, dA$$

$$= - \iint_A (\rho \hat{e} \, v_n) \, dA - \iint_A w_n \, dA - \iint_A q_n \, dA \quad \text{(E-13)}$$

where v_s is the velocity of any surface element, and subscript n indicate the component of vector normal to the surface. Rearrangement of this expression gives

$$\frac{d}{dt} \iiint_V \rho \hat{e} \, dV$$

$$= - \iint_A \rho \hat{e} \, [v_n - v_{s,n}] \, dA - \iint_A w_n \, dA - \iint_A q_n \, dA \quad \text{(E-14)}$$

From equation (E-5),

$$\vec{v}_r = \vec{v}_n - \vec{v}_{s,n} \, ,$$

and thus, equation (E-14) becomes

$$\frac{d}{dt} \iiint_V \rho \hat{e} \, dV$$

$$= - \iint_A \rho \hat{e} \, v_{r,n} \, dA - \iint_A w_n \, dA - \iint_A q_n \, dA \quad \text{(E-15)}$$

The work flux, w_n, can be divided into three parts, i.e.,

$$w_n = w_{f,n} + w_{u,n} + w_{0,n} \quad \text{(E-16)}$$

where w_f is the flux of work performed by the flowing material, w_u the

work flux between the system under consideration and other systems

including mechanical work, electric work, magnetic work, etc., and w_0

the flux of work lost though the surface to the surroundings. Consider-

ing that w_f is essentially the pressure work, we have

$$\iint_A w_n \, dA = \iint_A w_{f,n} \, dA + \iint_A w_{u,n} \, dA + \iint_A w_{0,n} \, dA$$

$$= \iint_A P \, v_{r,n} \, dA + \iint_A w_{u,n} \, dA + \iint_A w_{0,n} \, dA \quad \text{(E-17)}$$

The heat flux, q, can be divided into two parts, one representing heat

flux between system A and any one of other systems, q_u, and the other

representing flux of heat lost through the boundary of system A to the

surroundings, q_0. Thus, we have

$$\iint_A q_n \, dA = \iint_A q_{u,n} \, dA + \iint_A q_{0,n} \, dA \quad \text{(E-18)}$$

Substitution of equation (E-17) and (E-18) into equation (E-15)

gives

$$\frac{d}{dt} \iiint_V \rho \hat{e} \, dV$$

$$= - \iint_A \rho \hat{e} \, v_n \, dA$$

$$-(\iint_A P \, v_{r,n} \, dA + \iint_A w_{u,n} \, dA + \iint_A w_{0,n} \, dA)$$

$$-(\iint_A q_{u,n} \, dA + \iint_A q_{0,n} \, dA) \quad \text{(E-19)}$$

Upon rearrangement, we have

$$\frac{d}{dt} \iiint_V \rho \hat{e} \, dV$$

$$= - \iint_A \rho \, (\hat{e} + \frac{P}{\rho}) \, v_{r,n} \, dA - (\iint_A q_{u,n} \, dA + \iint_A q_{0,n} \, dA)$$

$$-(\iint_A w_{u,n} \, dA + \iint_A w_{0,n} \, dA) \quad \text{(E-20)}$$

Note that

$$\hat{e} + \frac{P}{\rho} = \hat{u} + \frac{P}{\rho} + \frac{v^2}{2} + gx + \ldots$$

$$= \hat{h} + \frac{v^2}{2} + gx + \ldots \tag{E-21}$$

where $\hat{u}$ is the specific internal energy, $\hat{h}$ the specific enthalpy, $\frac{v^2}{2}$ the kinetic energy per unit mass and gx the potential energy per unit mass; the dotted line in the right-hand side indicates that other forms of energy, such as the electric and magnetic energy, need be considered in general. Thus, equation (E-20) reduces to

$$\frac{d}{dt} \iiint\limits_{V} \rho \hat{e} \ dV$$

$$= - \iint\limits_{A} \rho (\hat{h} + \frac{v_n^2}{2} + gx + \ldots) \ v_{r,n} \ dA$$

$$- (\iint\limits_{A} q_{u,n} \ dA + \iint\limits_{A} q_{0,n} \ dA)$$

$$- (\iint\limits_{A} w_{u,n} \ dA + \iint\limits_{A} w_{0,n} \ dA) \tag{E-22}$$

Furthermore, note that

$$w_{0,n} = (w_P)_{0,n} + (w_x)_{0,n} \tag{E-23}$$

where $(w_P)_0$ denotes the flux of work lost against the surroundings due to the expansion of the surface of the system and $(w_x)_0$ the flux of work lost in any other forms, and thus, equation (E-22) can be rearranged as

$$\frac{d}{dt} \iiint\limits_{V} \rho \hat{e} \ dV + \iint\limits_{A} (w_P)_{0,n} \ dA$$

$$= - \iint\limits_{A} \rho (\hat{h} + \frac{v_n^2}{2} + gx + \ldots) \ v_{r,n} \ dA$$

$$- [\iint\limits_{A} q_{u,n} \ dA + \iint\limits_{A} q_{0,n} \ dA]$$

$$- [\iint\limits_{A} w_{u,n} \ dA + \iint\limits_{A} (W_x)_{0,n} \ dA] \tag{E-24}$$

As done in the section, ENERGY BALANCE, in Appendix A, we write the microscopic equation of energy for an unsteady-state open flow system at the dead state as

$$\frac{\partial}{\partial t} \rho \hat{e}_0 = -(\nabla \cdot \rho \hat{e} \; \vec{v}) - (\nabla \cdot \vec{w}_0) \qquad (E-25)$$

where subscript 0 denotes the dead state. Note that w_0 includes both the flux of work performed by the flowing materials, $(w_0)_f$, and the flux of work lost due to the expansion of the surface of the system, $(w_{0,p})_0$. By resorting to the Leibnitz formula and the Gauss-Ostrogradskii divergence theorem for equation (E-25), we have

$$\frac{d}{dt} \iiint_V \rho \hat{e}_0 \; dV + \iint_A (w_{0,p})_{0,n} \; dA$$

$$= - \iint_A \rho \hat{h}_0 \; v_{r,n} \; dA \qquad (E-26)$$

where $\hat{h}_0$ is the specific enthalpy at the dead state.

Subtracting each side of equation (E-26) from the corresponding term of equation (E-24), we have

$$\frac{d}{dt} \iiint_V \rho (\hat{e} - \hat{e}_0) \; dV + \iint_A [(w_p)_{0,n} - (w_{0,p})_{0,n}] \; dA$$

$$= - \iint_A \rho [(\hat{h} - \hat{h}_0) + \frac{v_n^2}{2} + gx + \ldots] \; v_{r,n} \; dA$$

$$-[\iint_A q_{u,n} \; dA + \iint_A q_{0,n} \; dA]$$

$$-[\iint_A w_{u,n} \; dA + \iint_A (w_x)_{0,n} \; dA] \qquad (E-27)$$

By defining the specific enthalpy relative to the dead state, $\hat{\beta}$, as (see, e.g., Szargut and Petela, 1965; Rodriguez, 1980; Fan and Shieh, 1980)

$$\hat{\beta} = \hat{h} - \hat{h}_0 \qquad (E-28)$$

equation (E-27) becomes

$$\frac{d}{dt} \iiint\limits_V \rho(\hat{e} - \hat{e}_0) \; dV + \iint\limits_A \; [(W_P)_{0,n} - (w_{0,P})_{0,n}] \; dA$$

$$= - \iint\limits_A \rho(\hat{\beta} + \frac{v_n^2}{2} + gx + \ldots) \; v_{r,n} \; dA$$

$$-[\iint\limits_A q_{u,n} \; dA + \iint\limits_A q_{0,n} \; dA]$$

$$-[\iint w_{u,n} \; dA + \iint (w_x)_{0,n} \; dA] \qquad \text{(E-29)}$$

This is the macroscopic expression of the energy balance with the energy contents measured relative to the dead state.

Similar to the mass balance, applying equation (E-29) to the system shown in Fig. A-1, whose state is a function of time, t, we have

$$\frac{d}{dt} [E_A(t) - (E_0)_A(t)] + [|(W_P)_0(t)| - |(W_{0,P})_0(t)|]$$

$$= \sum_i \left\{ \sum_k [\hat{\beta}(t) + \frac{v_n(t)^2}{2} + gx(t) + \ldots]_k \; (Mw)_k \; n_k(t) \right\}_i$$

$$- \sum_e \left\{ \sum_k [\hat{\beta}(t) + \frac{v_n(t)^2}{2} + gx(t) + \ldots]_k \; (Mw)_k \; n_k(t) \right\}_e$$

$$- \sum_\ell \left\{ \sum_k [\hat{\beta}(t) + \frac{v_n(t)^2}{2} + gx(t) + \ldots]_k \; (Mw)_k \; n_k(t) \right\}_\ell$$

$$+ |Q_1(t)| - |Q_2(t)| - |Q_0(t)|$$

$$+ |W_1(t)| - |W_2(t)| - |(W_x)_0(t)| \qquad \text{(E-30)}$$

Since

$$\int\limits_0^t |(W_P)_0(t)| \; dt = P_0[V_{A2}(t) - V_{A1}]$$

and

$$\int\limits_0^t |(W_{0,P})_0(t)| \; dt = P_0[(V_0)_{A2}(t) - (V_0)_{A1}]$$

and thus, integration of equation (E-30) over the time interval, ranging

from 0 to t, yields the energy balance around system A corresponding to equation (A-17) in appendix A or equation (2) in Chapter 3.

ENTROPY BALANCE

The entropy balance for an isolated overall system, including the small volume element, the heat source or sink and the surroundings, can be expressed as (see, e.g., Boder and Kenyon, 1980)

$$\frac{\partial}{\partial t} \rho\hat{s} = -(\nabla \cdot \rho\hat{s}\vec{v}) - (\nabla \cdot \frac{\vec{q}}{T}) + \sigma_s \qquad (E\text{-}31)$$

where $\hat{s}$ is the specific entropy, σ_s the rate of entropy creation in a unit volume. The integration of this equation over the volume, V, gives rise to

$$\iiint_V \frac{\partial}{\partial t} \rho\hat{s} \; dV = - \iiint_V (\nabla \cdot \rho\hat{s}\vec{v}) \; dV - \iiint_V (\nabla \cdot \frac{\vec{q}}{T}) \; dV$$
$$+ \iiint_V \sigma_s \; dV \qquad (E\text{-}32)$$

Applying the Leibnitz formula and the Gauss-Ostrogradskii divergence theorem to the left-hand and right hand sides of this equation, respectively, we have, after rearrangement,

$$\frac{d}{dt} \iiint_V \rho\hat{s} \; dV$$

$$= - \iint_A \rho\hat{s} \; (v_n - v_{s,n}) \; dA - \iint_A \frac{q_n}{T} \; dA$$
$$+ \iiint \sigma_s \; dV \qquad (E\text{-}33)$$

By resorting to equations (E-5) and (E-18), this expression can be written as

$$\frac{d}{dt} \iiint_V \rho \hat{s} \; dV$$

$$= - \iint_A \rho \hat{s} \, v_{r,n} \; dA - (\iint_A \frac{q_{u,n}}{T_u} \; dA - \iint_A \frac{q_{0,n}}{T_0} \; dA)$$

$$+ \iiint \sigma_s \; dV \qquad\qquad (E\text{-}34)$$

where T_u is the temperature of the heat source or sink and T_0 the temperature of the surroundings.

Similar to the energy balance, for the isolated overall system under consideration, the entropy balance at the dead state can be expressed as

$$\frac{\partial}{\partial t} \rho \hat{s}_0 = -(\nabla \cdot \rho \hat{s}_0 \vec{v}) \qquad\qquad (E\text{-}35)$$

where subscript 0 denotes the dead state. Note that at the dead state

$$\sigma_s = 0$$

because the process at the dead state is considered to be reversible. By employing Leibnitz formula and the Gauss-Ostrogradskii divergence theorem, equation (E-35) can be transformed into

$$\frac{d}{dt} \iiint_V \rho \hat{s}_0 \; dV = - \iint_A \rho \hat{s}_0 \, v_{r,n} \; dA \qquad\qquad (E\text{-}36)$$

Subtracting each side of equation (E-36) from the corresponding term of equation (E-34) yields

$$\frac{d}{dt} \iiint_V \rho (\hat{s} - \hat{s}_0) \; dV$$

$$= - \iint_A \rho (\hat{s} - \hat{s}_0) \, v_{r,n} \; dA$$

$$-(\iint_A \frac{q_{u,n}}{T_u} \; dA + \iint \frac{q_{0,n}}{T_0} \; dA)$$

$$+ \iiint_V \sigma_s \; dV \qquad\qquad (E\text{-}37)$$

The specific entropy relative to the dead state is defined as (see, e.g., Szargut and Petela, 1965; Fan and Shieh, 1980)

$$\hat{\gamma} \equiv \hat{s} - \hat{s}_0 \qquad (E\text{-}38)$$

Substitution of this expression into the right-hand side of equation (E-37) gives

$$\frac{d}{dt} \iiint \rho(\hat{s} - \hat{s}_0) \, dV$$

$$= - \iint_A \rho\hat{\gamma} \, v_{r,n} \, dA - \left(\iint_A \frac{q_{u,n}}{T_u} \, dA + \iint_A \frac{q_{0,n}}{T_0} \, dA \right)$$

$$+ \iiint \sigma_s \, dV \qquad (E\text{-}39)$$

This expression is the macroscopic entropy balance with the entropy contents measured relative to the dead state.

Applying equation (E-39) to the system depicted in Fig. A-4, whose state is a function of time, t, we have, after rearrangement,

$$\sigma(t) = \frac{d}{dt} \left[S_A(t) - (S_0)_A(t) \right]$$

$$- \sum_i \left[\sum_k \hat{\gamma}_k(t) \, (Mw)_k \, n_k(t) \right]_i$$

$$+ \sum_e \left[\sum_k \hat{\gamma}_k(t) \, (Mw)_k \, n_k(t) \right]_e$$

$$+ \sum_\ell \left[\sum_k \hat{\gamma}_k(t) \, (Mw)_k \, n_k(t) \right]_\ell$$

$$+ \left[- \frac{|Q_1(t)|}{T_{m1}} + \frac{|Q_2(t)|}{T_{m2}} + \frac{|Q_0(t)|}{T_0} \right] \qquad (E\text{-}40)$$

Integration of this equation over the time interval, ranging from 0 to t, gives rise to the entropy balance around system A corresponding to equation (A-26) in appendix A or equation (7) in Chapter 3.

AVAILABLE ENERGY BALANCE

The macroscopic available energy balance around the system can be obtained by multiplying the entropy balance, equation (E-39), by T_0 and subtracting the resultant from the energy balance, equation (E-29),

$$\frac{d}{dt} \iiint_V \rho(\hat{e} - \hat{e}_0) \, dV + \iint_A [(w_P)_{0,n} - (w_{0,P})_{0,n}] \, dA$$

$$- \frac{d}{dt} \iiint_V T_0 \, \rho(\hat{s} - \hat{s}_0) \, dV$$

$$= - \iint_A \rho[(\hat{\beta} - T_0 \, \hat{\gamma}) + \frac{v_n^2}{2} + gx + \ldots] \, v_{r,n} \, dA$$

$$- \iint_A q_{u,n} \, (1 - \frac{T_0}{T_u}) \, dA - \iint_A w_{u,n} \, dA$$

$$- \iint_A (w_x)_{0,n} \, dA - \iiint_V T_0 \, \sigma_s \, dV \qquad \text{(E-41)}$$

By defining the specific exergy, $\hat{e}$, as (see, e.g., Gaggioli, 1961; Szargut and Petela, 1965; Riekert, 1974; Fan and Shieh, 1980)

$$\hat{\varepsilon} \equiv (\hat{h} - \hat{h}_0) - T_0(\hat{s} - \hat{s}_0)$$

$$= \hat{\beta} - T_0 \, \hat{\gamma} \qquad \text{(E-42)}$$

equation (E-41) becomes, after rearrangement,

$$\frac{d}{dt} \iiint_V \rho[(\hat{e} - \hat{e}_0) - T_0(\hat{s} - \hat{s}_0)] \, dV$$

$$+ \iint_A [(w_P)_{0,n} - (w_{0,P})_{0,n}] \, dA$$

$$= - \iint_A \rho(\hat{\varepsilon} + \frac{v_n^2}{2} + gx + \ldots) \, v_{r,n} \, dA$$

$$- \iint_A q_{u,n} \, (1 - \frac{T_0}{T_u}) \, dA - \iint_A w_{u,n} \, dA$$

$$- [\iint_A (w_x)_{0,n} \, dA + \iiint_V (T_0 \, \sigma_s) \, dV] \qquad \text{(E-43)}$$

This is the macroscopic expression of the available energy balance.

Applying this equation to the system shown in Fig. A-1, whose state is a function of time, t, we have

$$\frac{d}{dt} \left\{ [E_A(t) - (E_0)_A(t)] - T_0[S_A(t) - (S_0)_A(t)] \right\}$$

$$+ \left| (W_P)_0(t) \right| - \left| (W_{0,P})_0(t) \right|$$

$$= \sum_i \left\{ \sum_k [\hat{\epsilon}(t) + \frac{v_n(t)^2}{2} + gx(t) + \ldots]_k \ (Mw)_k \ n_k(t) \right\}_i$$

$$- \sum_e \left\{ \sum_k [\hat{\epsilon}(t) + \frac{v_n(t)^2}{2} + gx(t) + \ldots]_k \ (Mw)_k \ n_k(t) \right\}_e$$

$$- \sum_\ell \left\{ \sum_k [\hat{\epsilon}(t) + \frac{v_n(t)^2}{2} + gx(t) + \ldots]_k \ (Mw)_k \ n_k(t) \right\}_\ell$$

$$+ \left| Q_1(t) \right| \ (1 - \frac{T_0}{T_{m1}}) - \left| Q_2(t) \right| \ (1 - \frac{T_0}{T_{m2}})$$

$$+ \left| W_1(t) \right| - \left| W_2(t) \right|$$

$$- [\left| (W_x)_0(t) \right| + (T_0 \ \sigma(t))] \tag{E-44}$$

Since

$$\int_0^t \left| (W_P)_0(t) \right| \ dt = P_0[V_{A2}(t) - V_{A1}]$$

and

$$\int_0^t \left| (W_{0,P})_0(t) \right| \ dt = P_0[(V_0)_{A2}(t) - (V_0)_{A1}(t)],$$

integration of equation (E-44) over the time interval, ranging from 0 to t, gives rise to the available energy balance, corresponding to equation (A-29) in appendix A or equation (11) in Chapter 3.

NOMENCLATURE

A $\qquad$ = system A

a $\qquad$ = unit area of the control surface, m^2

E $\qquad$ = total internal energy, J

e $\qquad$ = output streams

$\hat{e}$ $\qquad$ = total internal energy per unit mass, J/kg

gx $\qquad$ = specific potential energy, J/kg

$\hat{h}$ $\qquad$ = enthalpy per unit mass, J/kg

i $\qquad$ = input streams

j $\qquad$ = molar flux, kmol/sec $\cdot$ m^2

k $\qquad$ = material species

ℓ $\qquad$ = leakage

M $\qquad$ = mass, kg

Mw $\qquad$ = molecular weight, kg/kmol

n $\qquad$ = subscript standing for the component of the vector normal to the surface

n_k $\qquad$ = molar flow rate including both convective and diffusional flows of substance k, kmol/sec

P $\qquad$ = pressure, atm

$|Q_0|$ $\qquad$ = heat loss to the envrionment per unit time, J/sec

$|Q_1|$ $\qquad$ = heat transmitted from system M1 to system A per unit time, J/sec

$|Q_2|$ $\qquad$ = heat transmitted from system A to system M2 per unit time, J/sec

$\vec{q}$ $\qquad$ = vector representing heat flux, J/sec $\cdot$ m^2

q_u $\qquad$ = flux of usable heat, J/sec $\cdot$ m^2

q_0 $\qquad$ = flux of heat loss, J/sec $\cdot$ m^2

S $\qquad$ = entropy, J/K

$\hat{s}$ $\qquad$ = entropy per unit mass, J/K $\cdot$ kg

T = temperature of system A, K

T_{m1} = temperature of system M1, K

T_{m2} = temperature of system M2, K

T_u = temperature of the heat source or sink, T

t = time, sec

$v_n^2/2$ = specific kinetic energy, J/kg

$\hat{u}$ = internal energy per unit mass, J/kg

V = volume, m^3

$\vec{v}$ = vector representing the fluid velocity, m/sec

v_r = relative velocity, m/sec

v_s = velocity of any surface element, m/sec

$|W_0|$ = work loss to the surroundings per unit time, J/sec

$|W_1|$ = work supplied from system N1 to system A per unit time, J/sec

$|W_2|$ = work supplied from system A to system N2 per unit time, J/sec

$|(W_x)_0|$ = work loss to the environment except that due to the expansion of the boundaries of system A per unit time, J/sec

$\vec{w}$ = vector representing work flux, J/sec $\cdot$ m^2

w_0 = flux of work loss, J/sec $\cdot$ m^2

w_f = flux of work performed by the flowing material, J/sec $\cdot$ m^2

$(w_P)_0$ = flux of work lost against the surroundings due to the expansion of the surface of the system, J/sec $\cdot$ m^2

w_u = flux of usable work, J/sec $\cdot$ m^2

$(w_x)_0$ = flux of work lost to the environment except that due to the expansion of the surface of the system, J/sec $\cdot$ m^2

x_k = mole fraction of substance k

GREEK

$\hat{\beta}$ = enthalpy relative to the dead state per unit mass, J/kg

$\hat{\gamma}$ = entropy raltive to the dead state per unit mass, J/K · kg

$\hat{\epsilon}$ = exergy per unit mass, J/kg

ρ = density, kg/m^3

σ_s = created entropy per unit mass, J/K · sec

Ω = control surface

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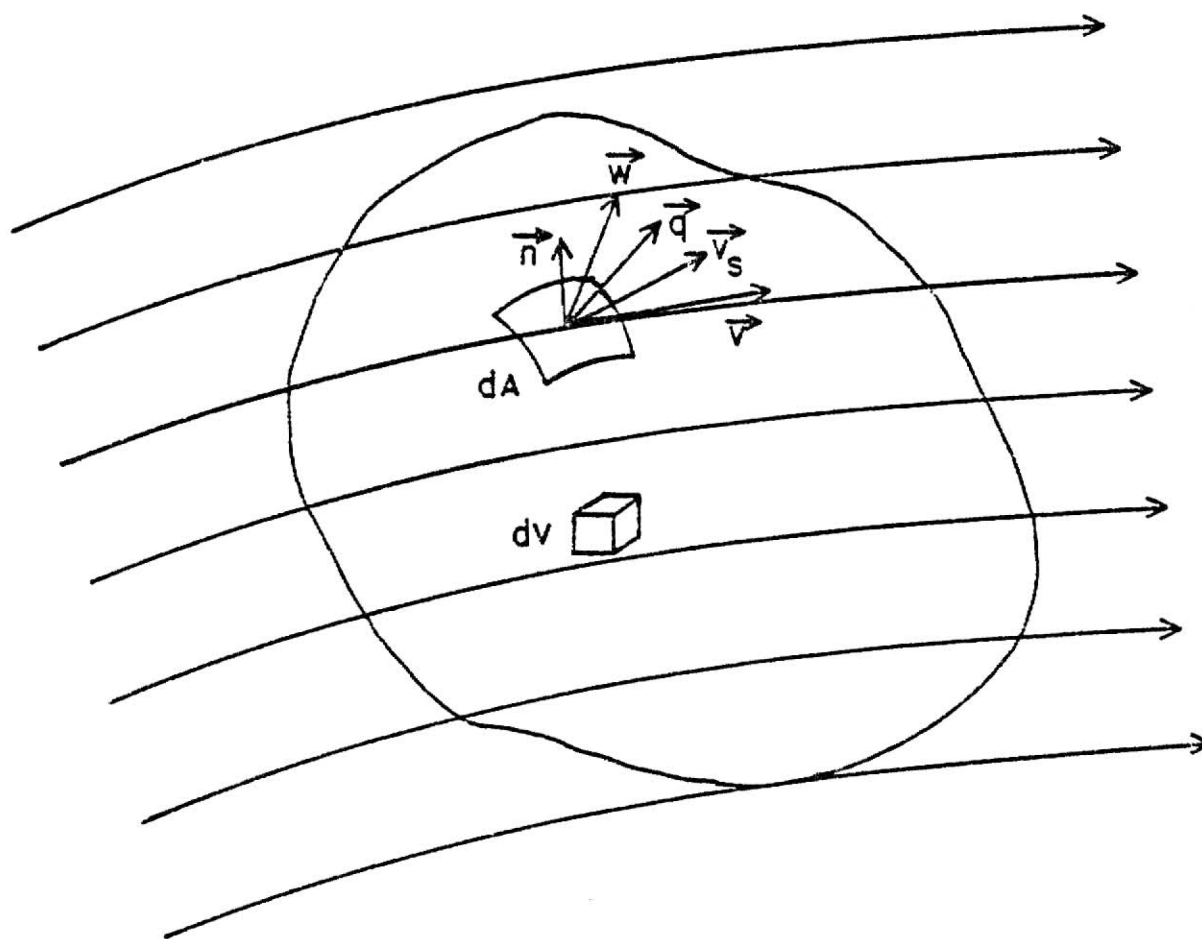White, F. M., Fluid Mechanics, McGraw-Hill, New York, 1979.

Fig. E-1. Diagram of an unsteady-state
open flow system.

THERMODYNAMIC ANALYSIS
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by

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ABSTRACT

Growing awareness of limited energy supplies has prompted a great
deal of effort in developing and designing energy-efficient process
systems; consequently, analyzing such systems from the thermodynamic
point of view has become increasingly important. One of the most important
recent developments in classical thermodynamics is establishment of the
so-called single axiom approach in which the first law, second law and
other laws and corollaries of classical thermodynamics can be deduced from
a single basic law of stable equilibrium. The single axiom implies directly
the existence of irreversibility in natural processes, indicating the neces-
sity of evaluating the degree of thermodynamic irreversibility in system
analysis.

A systematic procedure for analyzing a process system has been intro-
duced, based on the law of mass conservation, and the first and second laws
of thermodynamics, leading to the energy and available energy balances for
the system. The procedure enables us to evaluate the thermodynamic first-
law and second-law efficiencies and to identify the nature and sources of the
thermodynamic inefficiency or irreversibility of the system. The use of the
procedure has been illustrated with several examples in the area of energy
conservation and conversion; specifically, a counter-current heat exchanger,
a biomass pyrolysis process and an anaerobic sludge digestion process have
been systematically analyzed.