# ChE curriculum

# ENERGY CONSUMPTION VS. ENERGY REQUIREMENT

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oday, the phrase "energy consumption" is popularly spoken and written.<sup>[1]</sup> Nevertheless, caution should be exercised for its continued use, especially in the instruction of not only thermodynamics but also various other courses in engineering, including those in chemical engineering.

The first law of thermodynamics teaches that energy is always conserved in an isolated (or closed) system; it is neither created nor destroyed by any process, system, or phenomenon.<sup>[2-5]</sup> In contrast, the available energy analysis, which is the combination of the first and second laws of thermodynamics, indicates that in the real world the available energy is *never* conserved, even in an isolated (or closed) system. Even though in ideal circumstances available energy is only *theoretically* conserved, the reality is that it is incessantly consumed, or dissipated, by any process, system, or phenomenon.<sup>[6-15]</sup>

This consumption of available energy—or exergy— is accompanied by an increase in entropy, signifying the dissipation of available energy (or exergy) to the surrounding environments. The dissipation of this available energy (exergy) reduces its potential or availability to perform useful work.

Similar to enthalpy, exergy is a state property of any system. The enthalpy as well as exergy contents of materials are



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# MASS, ENERGY, AND AVAILABLE ENERGY BALANCES

A system in which a phenomenon or process of interest occurs is thermodynamically defined or specified by its mass, energy, and available energy balances.<sup>[8, 11, 13, 19-21]</sup> The following subsections outline these three balances for system A, or simply "the system," having multiple input and output streams under the steady-state, open-flow conditions depicted in Figure 1, on the basis of a unit time, *i.e.*, the rate. Figure 1 exhibits an isolated overall system; besides system A, it encom-

passes work and heat sources and sinks, and the entire surroundings, *i.e.*, environments. It is postulated that, except *energy* (enthalpy) and *available energy* (exergy) of mass flowing through system A, other forms of energy—such as potential energy and kinetic energy—are negligible. Thus, the changes in the enthalpy and exergy are induced by the *transfer of energy* (between system A and its surroundings or other systems) as heat or work. For simplicity, the aforementioned three balances will be written around system A by referring to Figure 1 and with the notations given in the section on nomenclature.

# Mass Balance

By taking into account both convective and diffusional flows, the mass balance around system A yields

$$\sum_{i} M_{i} = \sum_{e} M_{e} \tag{1}$$

In terms of the molar flow rate, the above expression can be rewritten as

$$\sum_{i} \left[ \sum_{k} (M_{w})_{k} n_{k} \right]_{i} = \sum_{e} \left[ \sum_{k} (M_{w})_{k} n_{k} \right]_{e}$$
(2)



Figure 1. Schematic diagram of an isolated overall system encompassing a steady-state, open-flow system (system A), a heat source at temperature  $T_{_{m1}}$  (system Ml), a heat sink at temperature T<sub>m2</sub> (system M2), a work source (system Nl), a work sink (system N2), and the entire surroundings at the environmental temperature of T<sub>o</sub> and the environmental pressure of  $P_{o}$ . In the text, entering streams  $B_1, B_2, \ldots$  are designated by subscript i; and exiting streams  $C_1, C_2, \ldots, L$ —the last being the leaking stream (leakage)—are designated by subscript e; the useful and leaking streams among the exiting streams are differentiated by additional subscripts u and l, respectively.

#### Energy Balance

The energy balance around system A yields

$$\left\{ \left[ \sum_{i} \left( \sum_{k} \overline{\beta}_{k} n_{k} \right)_{i} \right] + \left[ |W_{1}| + |Q_{1}| \right] \right\}$$
$$= \left\{ \left[ \sum_{e} \left( \sum_{k} \overline{\beta}_{k} n_{k} \right)_{e} \right] + \left[ |W_{2}| + |Q_{2}| \right] + \left[ \left| (W_{x})_{0} \right| + |Q_{0}| \right] \right\}$$
(3)

Even under steady-state flow conditions, some parts of the system, such as the surface of a rotating shaft of any pump, do the work against the surroundings, or continuously generate electric charges which are discharged to the surroundings. This leads to the work loss,  $|(W_x)_0|$ , which will be transformed into thermal energy and be transferred to the surroundings as heat. The term,  $|(W_x)_0|$ , therefore, can be combined with the heat loss,  $|Q_0|$ , thereby constituting the total heat loss to the surroundings,  $|Q_{0w}|$ ; thus,

$$|Q_{0w}| = |Q_0| + |(W_x)_0|$$

This renders it possible to rewrite Eq. (3) as

$$\begin{cases} \left[\sum_{i} \left(\sum_{k} \overline{\beta}_{k} n_{k}\right)_{i}\right] + \left[|W_{1}| + |Q_{1}|\right] \\ = \left\{ \left[\sum_{e} \left(\sum_{k} \overline{\beta}_{k} n_{k}\right)_{e}\right] + \left[|W_{2}| + |Q_{2}|\right] + |Q_{0w}| \right\} \end{cases}$$
(4)

Note that the energy content of the isolated overall system remains invariant regardless of whether the analysis for system A is under steady-state or unsteady-state flow conditions.

#### Entropy Balance

The principle of the increase of entropy, which is a mani-

Figure 2. Schematic diagram of a steady-state thermal mixing system, where a stream of water at 373 K and 1atm entering the system at the rate of 0.5 kg·s<sup>-1</sup> is mixed adiabatically and isobarically with another stream of water at 273 K and 1 atm entering the system at the rate of 0.5 kg · s<sup>-1</sup>; the resultant stream of water exits from the system at the rate of 1.0 kg·s<sup>-1</sup> at 1 atm and 323 K , resulting from the energy balance that yields  $\{(0.5 \times 1.0 \times 373 + 0.5 \times 1.0 \times 273)/$  $[(0.5 + 0.5) \times 1.0]\}.$ <sup>[13, 21]</sup> Surroundings  $(T_o, P_o)$ Stream 1,  $H_2O, 373 K$ Stream 2  $H_2O, 273 K$ Mixer

festation of the second law of thermodynamics, states: "The entropy of an isolated system increases or in the limit remains constant."<sup>[2, 16]</sup> Consequently,

$$\left(\frac{\mathrm{dS}}{\mathrm{dt}}\right)_{\mathrm{iso}} \ge 0$$

The above equation can be rewritten as<sup>[2]</sup>

$$\left(\Delta S\right)_{iso} \ge 0 \tag{5}$$

In this expression, subscript iso stands for the isolated system. The overall system depicted in Figure 1 is one such system as previously indicated: It encompasses system A and its surroundings. It is often convenient to transform Eq. (5) into an equality by introducing a nonnegative quantity,  $\sigma$ , defining the rate of entropy creation in the isolated overall system; this gives rise to

$$\left(\Delta S\right)_{iso} \equiv \sigma \tag{6}$$

By considering all the quantities that lead to the change in entropy, we obtain

$$(\Delta S)_{iso} = \sigma$$

$$= \left\{ \left[ \sum_{e} \left( \sum_{k} \bar{r}_{k} n_{k} \right)_{e} \right] + \frac{|Q_{2}|}{T_{m2}} \right\} - \left\{ \left[ \sum_{i} \left( \sum_{k} \bar{r}_{k} n_{k} \right)_{i} \right] + \frac{|Q_{1}|}{T_{m1}} \right\} + \frac{|Q_{0w}|}{T_{0}} \right\}$$

$$+ \frac{|Q_{0w}|}{T_{0}}$$
(7)

As indicated in connection with the energy balance,  $|Q_{0w}|$  in the above expression includes the work loss  $|(W_x)_0|$  as well as the heat loss  $|Q_0|$  to the surroundings.

#### Available Energy Balance

=

Combining the energy balance, Eq. (4), and the entropy creation, Eq. (7), gives rise to

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$$\begin{cases} \sum_{i} \left[ \sum_{k} \left( \overline{\beta} - T_{0} \overline{\gamma} \right)_{k} n_{k} \right]_{i} + \left[ |W_{1}| + |Q_{1}| \left( 1 - \frac{T_{0}}{T_{m1}} \right) \right] \end{cases} \tag{8} \\ = \left\{ \sum_{e} \left[ \sum_{k} \left( \overline{\beta} - T_{0} \overline{\gamma} \right)_{k} n_{k} \right]_{e} + \left[ |W_{2}| + |Q_{2}| \left( 1 - \frac{T_{0}}{T_{m2}} \right) \right] \right\} + T_{0} \sigma \end{cases}$$

In light of the aforementioned definitions of  $\overline{\beta}$  and  $\overline{\gamma}$ , term  $(\overline{\beta} - T_0 \overline{\gamma})$  in the above equation has a connotation of the available energy of molar species, for which symbol  $\overline{\epsilon}$  is coined; it is defined as the partial molar exergy. Thus,

$$\overline{\epsilon} = \beta - T_0 \overline{\gamma} \tag{9}$$

Hence, Eq. (8) can be rewritten as

=

$$\left\{ \left[ \sum_{i} \left( \sum_{k} \bar{\epsilon}_{k} n_{k} \right)_{i} \right] + \left[ |W_{1}| + |Q_{1}| \left( 1 - \frac{T_{0}}{T_{m1}} \right) \right] \right\}$$
(10)  
$$\left\{ \left[ \sum_{e} \left( \sum_{k} \bar{\epsilon}_{k} n_{k} \right)_{e} \right] + \left[ |W_{2}| + |Q_{2}| \left( 1 - \frac{T_{0}}{T_{m2}} \right) \right] \right\} + T_{0} \sigma$$

The quantities in the brace on the left-hand side of Eq. (10) have an implication of the total available energy input to system A. Note that they are not equal to the quantities in the brace on the right-hand side of Eq. (10) that have an implication of the total available energy exiting from the system. Their difference,  $T_0\sigma$ , signifies the available energy dissipated by all types of irreversibility, which is transferred as thermal energy or heat from the system to its surroundings under the environmental conditions, as elaborated earlier.

The partial molar enthalpy relative to the dead state,  $\beta$ , in Eq. (4), the partial molar entropy relative to the dead state,  $\bar{\gamma}$ , in Eq. (7), and the partial molar exergy relative to the dead state,  $\bar{\epsilon}$ , in Eq. (10) can be estimated from the following equations.<sup>[7-11, 17, 23]</sup>

$$\overline{\beta} = \overline{\beta}_{o} + \int_{T_{o}}^{T} \overline{c}_{p} dT + \int_{P_{o}}^{P} \left[ \overline{v} - T \left( \frac{\partial \overline{v}}{\partial T} \right)_{P} \right] dP$$
(11)

$$\bar{\gamma} = \bar{\gamma}_{o} + \int_{T_{o}}^{T} \frac{\bar{c}_{P}}{T} dT - \int_{P_{o}}^{P} T \left( \frac{\partial \bar{v}}{\partial T} \right)_{P} dP$$
(12)

$$\overline{\epsilon} = \overline{\epsilon}_{o} + \int_{T_{o}}^{T} \overline{c}_{P} \left( 1 - \frac{T_{o}}{T} \right) dT + \int_{P_{o}}^{P} \left[ \overline{v} - \left( T - T_{o} \right) \left( \frac{\partial \overline{v}}{\partial T} \right)_{P} \right] dP \qquad (13)$$

Many of their values can also be found in various sources.<sup>[11, 17, 22, 23]</sup>

## THE MIXER EXAMPLE

This illustration is based on an extremely simple example. It is well suited, however, for effectively conveying the main theme of the current contribution. This example is an extension of the well-known one<sup>[13, 21]</sup> in which: no work or heat is transferred from the system of concern to other systems and vice versa; no work or heat is lost from the system to its surroundings; no moving mechanical parts are visible on the system; and no changes in the chemical compositions of the streams passing through the system are detectable. Nevertheless, simply mixing two streams of water at different temperatures internally leads to significant reduction of the available energy (exergy) of the system. Figure 2 illustrates the system, which is a steady-state, thermal-mixing device, or simply "the mixer."

## Mass Balance

The term,  $\sum_{e,l} M_{e,l}$ , in the mass balance equation, Eq. (1),

vanish for the mixer; thus,

$$\sum_{i} M_{i} = M_{e,u} \quad or \quad M_{e,u} - \sum_{i} M_{i} = 0$$
(14)

Since  $M_{e,u} = 1.0 \text{ kg} \cdot \text{s}^{-1}$  and  $\sum_{i} M_{i} = 0.5 + 0.5 = 1.0 \text{ kg} \cdot \text{s}^{-1}$ , we have

$$M_{e,u} - \sum_{i} M_{i} = 1.0 - 1.0 = 0 \text{ kg} \cdot \text{s}^{-1}$$
 (15)

As expected, the mass is conserved in the mixer and its surroundings, collectively constituting the isolated overall system: Water entering the mixer from its surroundings,

$$\sum_{i} M_{i}$$
,

balances out exactly the water exiting from the mixer to its surroundings,  $M_{eu}$ .

#### Energy Balance

The terms, 
$$\sum_{e,d} (\beta n)_{e,d}$$
,  $\sum_{e,l} (\beta n)_{e,l}$ ,  $|W_1|$ ,  $|W_2|$ ,  $|Q_1|$ ,  $|Q_2|$ , and

 $|Q_{0w}|$ , in the energy balance equation, Eq. (4), vanish when applied to the mixer; thus,

$$\sum_{i} (\beta n)_{i} = (\beta n)_{e,u} \quad \text{or} \quad (\beta n)_{e,u} - \sum_{i} (\beta n)_{i} = 0$$
(16)

On the basis of mass flow M, instead of molar flow n, the terms in the above expression are evaluated as

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 $(\beta M)_{e_{11}} = (25.0)(1.0) = 25.0 \text{ kcal} \cdot \text{s}^{-1}$ , in which

$$\begin{split} \left(\beta\right)_{e,u} = & \beta_o + \int_{T_o}^{T} c_P dt + \int_{P_o}^{P} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP \\ = & 0 + (50.0 - 25.0)(1.0) + 0 = 25.0 \text{ kcal} \cdot \text{kg}^{-1} \end{split}$$

and similarly

$$\sum_{1} (\beta M)_{i} = (-25.0)(0.5) + (75.0)(0.5) = 25.0 \text{ kcal} \cdot \text{s}^{-1}$$

Consequently,

$$(\beta M)_{e,u} - \sum_{i} (\beta M)_{i} = 25.0 - 25.0 = 0 \text{ kcal} \cdot \text{s}^{-1}$$
 (17)

Obviously, the energy in the mixer and its surroundings collectively constituting the isolated overall system—remains unchanged; energy is conserved, *i.e.*, never consumed. The energy entering into the mixer from its surroundings with the flow of water,

$$\sum_{i} \bigl(\beta M\bigr)_{i}\,,$$

balances out the energy exiting from the mixer to its surroundings with the flow of water,  $(\beta M)_{e,u}$ . Naturally, the first-law efficiency of the mixer in terms of energy conservation is (25.0/25.0) or 100.0%.

# Entropy Balance

The terms,

$$\sum_{e,d} \left( \sum_{k} \gamma_{k} n_{k} \right)_{e,d}, \sum_{e,l} \left( \sum_{k} \gamma_{k} n_{k} \right)_{e,l}, \left| \frac{Q_{1}}{T_{m1}} \right|, \left| \frac{Q_{2}}{T_{m2}} \right|,$$

and  $|Q_{0w}|/T_0$ , in the expression for entropy creation, Eq. (7), vanish when applied to the mixer and its surroundings, *i.e.*, to the isolated overall system; thus,

$$(\Delta S)_{iso} = \sigma = (\gamma n)_{e,u} - \sum_{i} (\gamma n)_{i}$$
(18)

On the basis of mass flow M, instead of molar flow n, the terms in the right-hand side of the above expression are evaluated as

$$(\gamma M)_{e,u} = (0.080)(1.0) = 0.08 \text{ kcal} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$$

in which

$$(\gamma)_{e,u} = \gamma_o + \int_{T_o}^{T} \frac{c_P}{T} dT - \int_{P_o}^{P} T\left(\frac{\partial v}{\partial T}\right)_P dP$$
$$= 0 + 1 \cdot \ln\left(\frac{323}{298}\right) - 0 = 0.080 \text{ kcal} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$$

and similarly

$$\sum_{i} (\gamma M)_{i} = (-0.088)(0.5) + (0.224)(0.5) = 0.068 \text{ kcal} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$$

As a result, we have

$$(\Delta S)_{iso} = \sigma$$
$$= (\gamma M)_{e,u} - \sum_{i} (\gamma M)_{i}$$
$$= 0.012 \text{ kcal} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$$

or, equivalently expressed as the most diffused form of thermal energy under the environmental conditions,

$$T_0(\Delta S)_{iso} = T_0 \sigma$$
  
=(298)(0.012)  
= 3.576 kcal·s<sup>-1</sup>·K<sup>-1</sup> (19)

This ascertains that the entropy change of the isolated overall system, accompanying whatever process or phenomenon is occurring in the mixer, is destined to be nonnegative.

#### Available Energy Balance

The terms,

$$\sum_{e,d} \left( \sum_{k} \varepsilon_{k} n_{k} \right)_{e,d}, \sum_{e,l} \left( \sum_{k} \varepsilon_{k} n_{k} \right)_{e,l}, |W_{1}|, |W_{2}|, |Q_{1}| (1 - T_{0}/T_{m1}),$$

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and  $|Q_2|(1-T_0/T_{m2})$ , in the available energy balance equation, Eq. (10), vanish when applied to the mixer; thus,

$$\sum_{i} (\epsilon n)_{i} = (\epsilon n)_{e,u} + (T_{0}\sigma) \text{ or } (\epsilon n)_{e,u} - \sum_{i} (\epsilon n)_{i} = -(T_{0}\sigma) \quad (20)$$

On the basis of mass flow M, instead of molar flow n, the terms in the above expression are evaluated as

$$(\epsilon M)_{e,u} = (1.160)(1.0) = 1.160 \text{ kcal} \cdot \text{s}^{-1}$$

in which,

$$(\epsilon)_{e,u} = (\beta)_{e,u} - T_0(\gamma)_{e,u}$$
  
= (25.0) - (298)(0.088) = 1.160 kcal·kg<sup>-1</sup>

and similarly

$$\sum_{i} (\epsilon M)_{i} = (1.224)(0.5) + (8.248)(0.5) = 4.736 \text{ kcal} \cdot \text{s}^{-1}$$

Hence,

$$(\epsilon M)_{e,u} - \sum_{i} (\epsilon M)_{i} = 1.160 - 4.736 = -3.576 \text{kcal} \cdot \text{s}^{-1} = -(T_0 \sigma) (21)$$

Note that Eq. (21) is totally unlike Eqs. (15) and (17): Exergy is not conserved. No work is performed on the surroundings by water passing through the mixer and no heat is lost to the surroundings from water passing through the mixer. In fact, it is even assumed that the flow of water does not even encounter any friction during the passage through the mixer. Nevertheless, the available energy (exergy) entering into the mixer from its surroundings with the flow of water,

$$\sum_i \bigl(\epsilon M\bigr)_i\,,$$

does not balance with the available energy (exergy) exiting from the mixer to its surroundings with the flow of water,

$$(\varepsilon M)_{e,u}$$

In fact, it decreases, thereby correctly reflecting the irreversibility of the thermal mixing of two water streams inside the mixer. The difference signifies the dissipation of available energy, evaluated by Eq. (21) as  $-3.576 \text{ kcal} \cdot \text{s}^{-1}$ : Available energy (exergy) is always consumed, or dissipated, in the real world. Naturally, this dissipation of available energy is the only source of the entropy increase or creation in the isolated overall system, whose thermal equivalent is evaluated by Eq. (19) as  $+3.576 \text{ kcal} \cdot \text{s}^{-1}$ . In essence, the energy of water streams "available" to perform useful work is lost to its surroundings in the most diffused form—thermal energy under environmental conditions—which is totally unavailable to do any work. This results in entropy creation in the isolated overall system, which can be the universe itself. In drastic contrast to the first-law efficiency, the second-law efficiency in terms of available energy (exergy) conservation is merely (1.160/4.7361) or 24.5%.

Now suppose that the mixer is externally heated at the rate,  $|Q_1|$ , of 50 kcal·s<sup>-1</sup> by a heater at the temperature,  $T_{m1}$ , of 800 K. Naturally, the temperature and the corresponding energy (enthalpy) of water exiting from the mixer increase to 373 K and  $[1.0 \times (100-25)] \times 1.0 \text{ kcal} \cdot \text{s}^{-1}$ , *i.e.*, 75 kcal \cdot \text{s}^{-1}, respectively. The energy balance around the mixer yields the firstlaw efficiency of [75/(25+50)]×100% or 100%, thereby indicating that it is not affected by external heating. The concomitant change in the available energy (exergy) of water exiting from the mixer is from 1.160 kcal·s<sup>-1</sup> to [75–(298  $\times 0.224$ ] $\times 1.0$  kcal·s<sup>-1</sup>, *i.e.*, 8.248 kcal·s<sup>-1</sup>. This is obviously an increase rather than a decrease without external heating, thus indicating the possibility of enhancing the mixer's second-law efficiency. In reality, however, the opposite is the case: simply adding external heating reduces the second-law efficiency from 24.5% to  $\{8.248/[4.736+50\times(1-298/800)]\}\times$ 100%, i.e., 22.8%. Regarding the first law, Seider, et al.,[21] state, "... it can not even give a clue as to whether energy is being used efficiently . . . ." Moreover, according to Reistad and Gaggioli,<sup>[24]</sup> "The second-law efficiency is the performance parameter which indicates the true thermodynamic performance of the system."

# CONCLUDING REMARKS

With the aid of a deceptively simple example, it has been unequivocally demonstrated that energy *is* conserved, *i.e.*, never consumed; what is always consumed, or dissipated, is available energy (exergy), which is the essence of this brief contribution. This simple example also succinctly indicates that an attempt to rigorously assess the sustainability of any process or system should be based firmly upon the thermodynamics, in general, and the evaluation of the system's second-law efficiency based on available energy (exergy), in particular, as practiced in the EU community<sup>[25]</sup> and the Canton of Geneva in Switzerland.<sup>[26]</sup>

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#### NOMENCLATURE

- A system A
- $\overline{c}_P$  specific heat,  $J \cdot mol^{-1} \cdot K^{-1}$
- M mass flow rate including both convective and diffusional flows,  $kg \cdot s^{-1}$
- Mw molecular weight, g · mol-1
  - N molar flow rate including both convective and diffu-

sional flows, mol · s<sup>-1</sup>

- P pressure, atm
- $\left|Q_{0}\right|$  heat loss to the environment per unit time,  $J\cdot s^{\text{-1}}$  or kcal  $\cdot$   $s^{\text{-1}}$
- $\left|Q_{0w}\right|~$  total heat loss to the environment per unit time,  $J\cdot s^{\text{-1}}$  or  $kcal\cdot s^{\text{-1}}$ 
  - $\left| Q_1 \right|$  heat transmitted from system M1 to system A per unit time,  $J \cdot s^{-1}$  or kcal  $\cdot s^{-1}$
  - $|Q_2|$  heat transmitted from system A to system M2 per unit time,  $J \cdot s^{-1}$  or kcal  $\cdot s^{-1}$ 
    - S entropy,  $J \cdot K^{-1}$
    - $\overline{s}$  partial molar entropy,  $J \cdot mol^{-1} \cdot K^{-1}$
    - T temperature of system A, K
  - T<sub>m1</sub> temperature of system Ml, K
  - T<sub>m2</sub> temperature of system M2, K
    - v volume, m<sup>3</sup>
- $|W_0|$  work lost to the surroundings per unit time,  $J \cdot s^{-1}$  or kcal  $\cdot s^{-1}$
- $|W_1|$  work supplied from system N1 to system A per unit time,  $J \cdot s^{-1}$  or kcal  $\cdot s^{-1}$
- $|W_2|$  work supplied from system N2 to system A per unit time,  $J \cdot s^{-1}$  or kcal  $\cdot s^{-1}$
- $\left( W_x \right)_0 \middle| \begin{array}{l} \text{work lost to the surroundings except that due to} \\ \text{expansion of the boundary of system A per unit time,} \\ J \cdot s^{-1} \text{ or kcal} \cdot s^{-1} \end{array}$

#### Greek letters

- $\beta~$  partial molar enthalpy relative to the dead state,  $J\cdot mol^{\text{-1}}$  or  $kcal\cdot kg^{\text{-1}}$
- $\beta_0$  partial molar chemical enthalpy, J · mol<sup>-1</sup> or kcal · kg<sup>-1</sup>
- $\overline{\epsilon}$  partial molar exergy, J · mol<sup>-1</sup> or kcal · kg<sup>-1</sup>
- $\overline{\epsilon}_{0}$  partial molar chemical exergy, J  $\cdot$  mol<sup>-1</sup> or kcal  $\cdot$  kg<sup>-1</sup>
- $\bar{\gamma}~$  partial molar entropy relative to the dead state,  $J\cdot mol^{-1}\cdot k^{-1}$  or kcal  $\cdot$  kg^{-1}\cdot K^{-1}
- $\bar{\gamma}_{o}$  partial molar chemical entropy, J  $\cdot$  mol<sup>-1</sup>  $\cdot$  k<sup>-1</sup> or kcal  $\cdot$  kg<sup>-1</sup>·K<sup>-1</sup>
- $\sigma$  created entropy per unit time, J  $\cdot$  sec^{-1}  $\cdot$  k^{-1} or kcal  $\cdot$  sec^{-1}  $\cdot$  K^{-1}

#### Subscripts

- 0 dead state
- e,u useful output streams
  - i input streams
- iso isolated system
- k material species
- l leakage

#### Superscript

0 standard state

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# The Next Millennium in ChE

#### Inside the Cell

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combination of rational design and screening of mutant libraries will be used to create green fluorescent proteins with improved photophysical properties.

9. Genetically Targetable Labels for Light and EM • Roger Y. Tsien, Ph.D., principal investigator, University of California, San Diego

> A team from the University of California and the University of Illinois plans a series of approaches to generate fluorescent proteins with increased photostability and higher quantum yield, to explore quantum dot construction and targeting, and to further develop tetracysteine labeling techniques for light and electron microscopy. The team's plans also include exploring genetically targetable labels with long excited state lifetimes based on lanthanide and transition metal luminescence as well as directed evolution of fluorescent proteins to improve their photophysical properties. A major goal of this team is to enable direct visualization in the electron microscope of the same molecules that have been tagged, observed, and dynamically tracked in the light microscope.

Now that breakthroughs are under way to provide specific information on the functioning and control of organelles, a unique opportunity is evolving for chemical engineers to use this mechanistic information to design new integrated biocellular operations and processes.

It is likely that exceptional progress will be made in the next decade to reveal the physical chemical phenomena that govern the organization and behavior of the biochemical processing units within cells. Naturally then, new concepts of process design will emerge for the chemical/biochemical industry through the research efforts of biochemical engineers. As this knowledge becomes available it will be incorporated into the graduate-program courses in chemical engineering departments as an enhancement to courses such as systems biology, bio-MEMS, biochemical separations, bioprocess engineering, and pharmaceutical biotechnology. One can expect a dramatic evolution in process technology that will become an important capability for future chemical engineers, especially for high-value, low-volume products.

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