

Chapter 21

Entropy Considerations and Analysis

INTRODUCTION

The law of conservation of energy is defined by many as the first law of thermodynamics. Its application allows calculations of energy relationships associated with various processes. The second law of thermodynamics is referred to as the “limiting law.” Historically, the study of the second law was developed by individuals such as Carnot, Clausius and Kelvin in the middle of nineteenth century. This development was made purely on a macroscopic scale and is referred to as the “classical approach” to the second law.

Environmental concerns involving conservation of energy issues gained increasing prominence during and immediately after the OPEC oil embargo of 1973. In addition, global population growth has led to an increasing demand for energy. Although the use of energy has resulted in great benefits, the environmental and human health impact of this energy use has become a concern. One of the keys to reducing and/or eliminating this problem will be achieved through what has come to be referred to as meaningful energy conservation.

The first law of thermodynamics is a conservation law concerned with energy transformations. Regardless of the types of energy involved in processes—thermal, mechanical, electrical, elastic, magnetic, etc.—the change in the energy of a system is equal to the difference between energy input and energy output. The first law also allows free convertibility from one form of energy to another, as long as the overall quantity is conserved. Thus, this law places no restriction on the conversion of work into heat, or on its counterpart—the conversion of heat into work. However, the second law is another matter.

Chapter contents include:

Qualitative Review of the Second Law

Describing Equations

The Heat Exchanger Dilemma

Applications

The reader should note that flow arrangements for increased/optimum heat recovery receives additional treatment in Chapter 22 as well as in Part Four, particularly Illustrative Examples 27.12 and 28.11.

QUALITATIVE REVIEW OF THE SECOND LAW

The brief discussion of energy conversion above leads to an important second-law consideration—energy has “quality” as well as quantity. Because work is 100% convertible to heat whereas the reverse situation is not true, work is a more valuable form of energy than heat. Although it is not as obvious, it can also be shown through second law arguments that heat also has “quality” in terms of the temperature at which it is discharged from a system. The higher the temperature, the greater the possible energy transformation into work. Thus, thermal energy stored at high temperatures is generally more useful to society than that available at lower temperatures. While there is an immense quantity of energy stored in the oceans, for example, its present availability to society for performing useful tasks is quite low. This implies, as noted above, that thermal energy loses some of its “quality” or is degraded when it is transferred by means of heat transfer from one temperature to a lower one. Other forms of energy degradation include energy transformations due to frictional effects and electrical resistance. Such effects are highly undesirable if the use of energy for practical purposes is to be maximized.^(1–3)

The second law provides some means of measuring this energy degradation through a thermodynamic term referred to as entropy and it is the second law (of thermodynamics) that serves to define this important property. It is normally designated as S with units of energy per absolute temperature (e.g., Btu/°R or cal/K). Furthermore, entropy calculations can provide quantitative information on the “quality” of energy and energy degradation.^(2,3)

In line with the discussion regarding the “quality” of energy, individuals at home and in the workplace are often instructed to “conserve energy.” However, this comment, if taken literally, is a misnomer because energy is automatically conserved by the provisions of the first law. In reality, the comment “conserve energy” addresses only the concern associated with the “quality” of energy. If the light in a room is not turned off, energy is degraded although energy is still conserved; i.e., the electrical energy is converted to internal energy (which heats up the room). Note, however, that this energy transformation will produce a token rise in temperature of the room from which little, if any, “quality” energy can be recovered and used again (for lighting or other useful purposes).⁽¹⁾

There are a number of other phenomena that cannot be explained by the law of conservation of energy. It is the second law of thermodynamics that provides an understanding and analysis of these diverse effects. However, among these considerations, it is the second law that can allow the measuring of the aforementioned “quality” of energy, including its effect on the design and performance of heat exchangers.

DESCRIBING EQUATIONS

Key equations pertinent to entropy calculations and heat exchanger design receive treatment in this section.

If ΔS_{syst} and ΔS_{surr} represent the entropy change of a system and surroundings, respectively, it can be shown⁽¹⁻³⁾ that for a particular process (and as a consequence of the second law), the total entropy change ΔS_{tot} is given by:

$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} \geq 0 \quad (21.1)$$

In effect, the second law requires that for any real processes, the total entropy change is positive; the only exception is if the process is reversible (the driving force for heat transfer is at all times zero) and then:

$$(\Delta S_{\text{tot}})_{\text{rev}} = 0 \quad (21.2)$$

Thus, no real process can occur for which the total entropy change is zero or negative. The fundamental facts relative to the entropy concept are that the entropy change of a system may be positive (+), negative (-), or zero; the entropy change of the surroundings during this process may likewise be positive, negative, or zero.

To re-examine the concept of “quality” energy, consider the insulated space pictured in Figure 21.1(A)–(B). Space (A) contains air and steam that are separated; space (B) contains the resulting mixture when both components are mixed. Both spaces are insulated ($Q = 0$) in this closed system with no work term ($W = 0$), so that one can conclude from the first law ($Q + W = \Delta U$) that:

$$\begin{aligned} \Delta U &= 0 \\ U_A &= U_B; U \equiv \text{internal energy} \end{aligned} \quad (21.3)$$

Although the energy levels are the same, one notes that system (A) has the capability of doing useful work (because of the high-temperature high-pressure steam) while

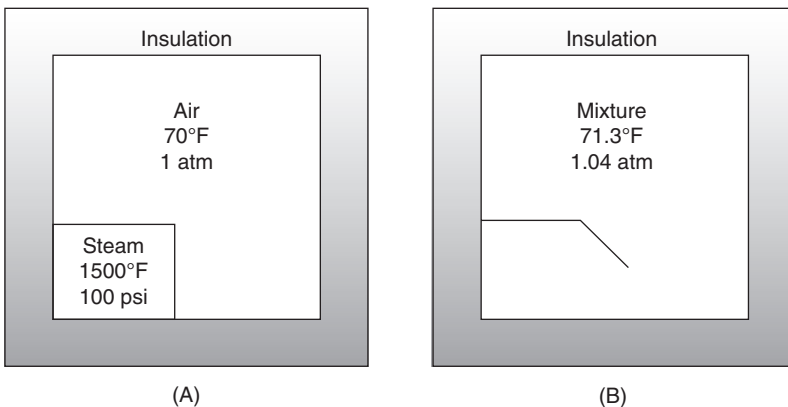


Figure 21.1 Entropy analysis.

system (B) does not. If an entropy analysis is performed (see later illustrative example) on both systems (A) and (B), one would deduce that (as noted earlier):

$$S_A < S_B \quad (21.4)$$

In effect, the entropy level has increased for the system that has lost its ability to do useful work due to the irreversible nature of the mixing process. It is in this manner that the concept of entropy can be used to determine a system's ability to either do useful work or lose its ability to do useful work. Thus, the second law leads to the conclusion that the greater the irreversibility of a process, the greater the (rate of) entropy increase and the greater the amount of energy that becomes unavailable for doing useful work.

Consider now the entropy change of gases. The entropy change of an ideal gas undergoing a change of state from pressure P_1 to P_2 at a constant temperature T is given by:

$$\Delta S_T = R \ln \left(\frac{P_1}{P_2} \right) \quad (21.5)$$

where R is the ideal gas law constant in consistent units. The entropy change of an ideal gas or liquid undergoing a change of state from T_1 to T_2 at a constant pressure is given by:

$$\Delta S_P = C_P \ln \left(\frac{T_2}{T_1} \right) \quad (21.6)$$

where C_P is the heat capacity at constant pressure in consistent units. Correspondingly, the entropy change for an ideal gas undergoing a change from (P_1, T_1) to (P_2, T_2) is:

$$\Delta S = R \ln \left(\frac{P_1}{P_2} \right) + C_P \ln \left(\frac{T_2}{T_1} \right) \quad (21.7)$$

Heat exchanger design equations are again reviewed in light of the development to follow. If \dot{Q} represents the rate of heat transfer between a hot and cold fluid flowing in a heat exchanger, application of the conservation on law for energy gives

$$\dot{Q}_H = \dot{m}_H c_{p,H} (T_{HI} - T_{HO}) \quad (21.8)$$

and

$$\dot{Q}_C = \dot{m}_C c_{p,C} (T_{CO} - T_{CI}) \quad (21.9)$$

where the subscripts H and C refer to the hot and cold fluids, respectively; I and O refer to the fluid inlet and outlet temperature, respectively; \dot{m} represents the mass flow rate, and c_p is once again the heat capacity at constant pressure (assumed constant). In addition, if there is no heat lost from the exchanger to the surroundings,

$$\dot{Q}_H = \dot{Q}_C \quad (21.10)$$

As noted numerous times earlier in the text, the following important equation relates \dot{Q} to the average temperature difference between the hot and cold fluids:

$$\dot{Q} = UA\Delta T_{lm} \quad (21.11)$$

This is the aforementioned heat exchanger design equation. The terms U , A , and ΔT_{lm} represent the overall heat transfer coefficient (a function of the resistance to heat transfer), the area for heat transfer, and the log mean temperature difference driving force (LMTD), respectively. For some exchangers, the latter term is given by

$$\Delta T_{lm} = \text{LMTD} = \frac{\Delta T_2 - \Delta T_1}{\ln(\Delta T_2/\Delta T_1)} \quad (21.12)$$

where ΔT_2 and ΔT_1 represent the temperature difference between the hot and cold fluid at each end of the exchanger, respectively. If $\Delta T_1 = \Delta T_2 = \Delta T$, then $\Delta T_{lm} = \Delta T$. For purposes of the analysis to follow, Equation (21.11) is rearranged in the form

$$\frac{\dot{Q}}{U\Delta T_{lm}} = A \quad (21.13)$$

THE HEAT EXCHANGER DILEMMA^(4,5)

One of the areas where the aforementioned meaningful energy conservation measures can be realized is in the design and specification of process (operating) conditions for heat exchangers. This can be best accomplished by the inclusion of second law principles in the analysis. The quantity of heat recovered in an exchanger is not alone in influencing size and cost. As the energy temperature difference driving force (LMTD) in the exchanger approaches zero, the “quality” heat recovered increases.

Most heat exchangers are designed with the requirements/specification that the temperature difference between the hot and cold fluid be at all times positive and be at least 20°F. This temperature difference or driving force is referred to by some as the approach temperature. However, and as it will be demonstrated in the Illustrative Examples to follow, the corresponding entropy change is also related to the driving force, with large temperature difference driving forces resulting in large irreversibilities and the associated large entropy changes.

The individual designing a heat exchanger is faced with two choices. He/she may decide to design with a large LMTD that results in both a more compact (smaller area) design (see Equation (21.13)) and a large entropy increase that is accompanied by the loss of “quality” energy. Alternately, a design with a small driving force results in both a larger heat exchanger and a smaller entropy change/larger recovery of “quality” energy.

Regarding the cooling medium for a given heat transfer duty, the design engineer has the option of circulating a large quantity with a small temperature change or a

small quantity with a large temperature change. The temperature change (or range) of the coolant affects the LMTD. If a large coolant quantity is used, the LMTD is larger and less heat transfer area A is required as a result of the large LMTD. Although this will reduce the original investment and fixed charges (capital and operating costs are discussed in Chapter 27), the amount of “quality” energy recovered will also be smaller, owing to the greater quantity of coolant employed. It is therefore apparent that an optimum must exist between the two choices: too much coolant, smaller surface, and the recovery of less “quality” energy *or* too little coolant, larger surface, and the recovery of more quality energy. In the limit, as the LMTD $\rightarrow 0$ the area requirement $A \rightarrow \infty$, the entropy change $\Delta S \rightarrow 0$ and the aforementioned recovered “quality” energy increases. Clearly, cost must be minimized, but just as clearly, the “quality” energy recovered must be included in the analysis. This dilemma is addressed below.

Consider first the modes of operation for the three heat exchangers shown in Figure 21.2. Note that for the purpose of analysis, $m_C = m_H = 1.0$ lb and $c_P = 1.0$ Btu/lb \cdot $^{\circ}$ F.

For operation (A):

$$\begin{aligned}\Delta T_{lm,A} &= 540 - 300 = 300 - 60 \\ &= 240^{\circ}\text{F}\end{aligned}$$

The entropy change for the hot fluid is

$$\begin{aligned}\Delta S_H &= m_H c_p \ln \frac{T_2}{T_1} \\ &= (1)(1) \ln \left(\frac{300 + 460}{540 + 460} \right) \\ &= \ln \left(\frac{760}{1000} \right) = -0.2744 \text{ Btu}/^{\circ}\text{R}\end{aligned}$$

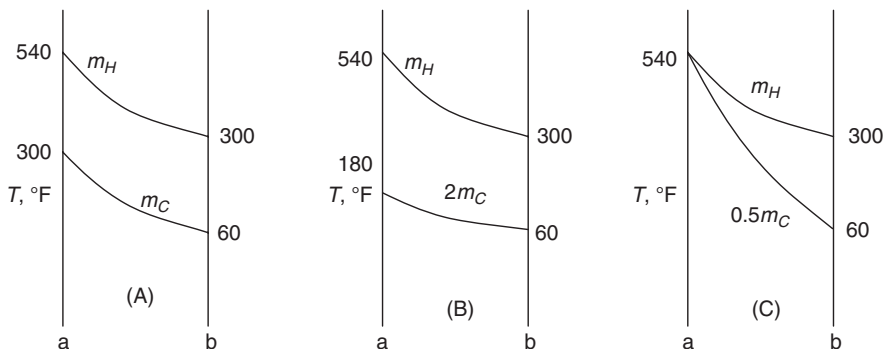


Figure 21.2 Heat exchanger operation.

and

$$\begin{aligned}\Delta S_C &= m_C c_p \ln\left(\frac{300 + 460}{540 + 460}\right) \\ &= \ln\left(\frac{760}{520}\right) \\ &= 0.3795 \text{ Btu}/^\circ\text{R}\end{aligned}$$

The total entropy increase is therefore

$$\begin{aligned}\Delta S_{T,A} &= -0.2744 + 0.3795 \\ &= 0.1054 \text{ Btu}/^\circ\text{R}\end{aligned}$$

For operation (B):

$$\begin{aligned}\Delta T_{lm,B} &= (360 - 240)/\ln(360/240) \\ &= 296^\circ\text{F}\end{aligned}$$

The entropy change can be calculated in a manner similar to that of operation (A):

$$\Delta S_H = -0.2744 \text{ Btu}/^\circ\text{R}$$

and,

$$\begin{aligned}\Delta S_C &= (2)(1) \ln\left(\frac{180 + 460}{60 + 460}\right) \\ &= 2 \ln\left(\frac{640}{520}\right) \\ &= 0.4153 \text{ Btu}/^\circ\text{R}\end{aligned}$$

The total entropy increase for operation (B) is therefore

$$\begin{aligned}\Delta S_{T,B} &= -0.2744 + 0.4153 \\ &= 0.1409 \text{ Btu}/^\circ\text{R}\end{aligned}$$

For operation (C):

$$\begin{aligned}\Delta T_{lm} &= 240/\infty \\ &= 0^\circ\text{F}\end{aligned}$$

The entropy change for the hot fluid is again

$$\Delta S_H = -0.2744 \text{ Btu}/^\circ\text{R}$$

while

$$\begin{aligned}\Delta S_C &= (0.5)(1) \ln\left(\frac{540 + 460}{60 + 460}\right) \\ &= (0.5) \ln\left(\frac{1000}{520}\right) \\ &= 0.3270 \text{ Btu}/^\circ\text{R}\end{aligned}$$

The total entropy change for (C) is therefore

$$\begin{aligned}\Delta S_{T,C} &= -0.2744 + 0.3270 \\ &= 0.0526 \text{ Btu}/^\circ\text{R}\end{aligned}$$

A summary of the results for operation A, B, and C plus the heat exchanger area requirement (A) and quality energy (QE) analysis is provided in Table 21.1.

One concludes that as the ΔT_{lm} (or LMTD) increases, the area requirement decreases (see Equation (21.13)); however, the QE available correspondingly decreases. Alternatively, if ΔT_{lm} decreases, both A and QE increase.

Consider now the operation of heat exchangers A and B , as provided in Figure 21.3. For Case I, one notes, using the same analysis as above, that

$$\begin{aligned}\text{LMTD}_A &= \text{LMTD}_B \\ A_A &= A_B; A_A = A_B = A \\ \Delta S_A &= \Delta S_B\end{aligned}$$

End result: Two m_C streams (m_{CA} and m_{CB}) are heated to 300°F where $m_{CA} = m_{CB} = m_C$. Two m_H streams are cooled to 300°F where $m_{HA} = m_{HB} = m_H$.

Consider Case II described by Figure 21.4. Here the coolant discharge from exchanger C serves as the inlet coolant to exchanger D . For Case II, one notes that

$$\begin{aligned}\text{LMTD}_C &> \text{LMTD}_D; \quad \text{LMTD}_D = 0 \\ A_C &< A_D; \quad A_D = \infty \\ \Delta S_C &> \Delta S_D; \quad \Delta S_D = 0\end{aligned}$$

Table 21.1 Heat Exchanger-Entropy Analysis Results

	$\Delta T_{lm}, ^\circ\text{F}$	$\Delta S_T, \text{Btu}/^\circ\text{R}$	A	QE
Operation A	0.1054	240	Moderate	Moderate
Operation B	0.1409	296	Lower	Lower
Operation C	0.0526	0	∞	Higher

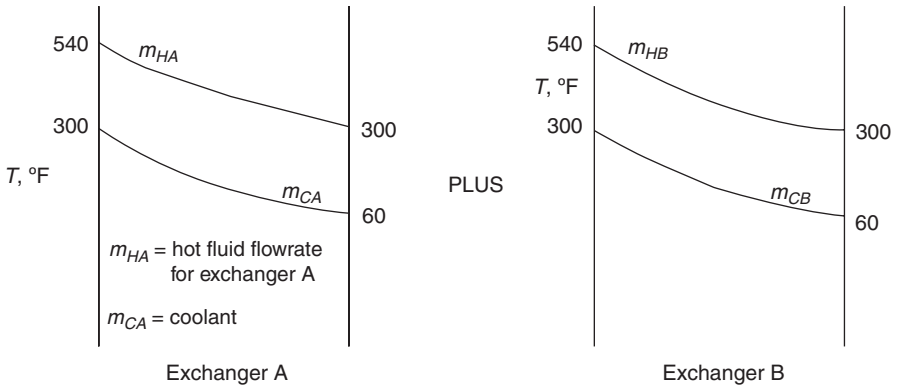


Figure 21.3 Heat exchanger comparison; Case I.

Also,

$$LMTD_A = LMTD_B = LMTD_C$$

$$A_A = A_B = A_C$$

End result: One m_C (m_{CC}) results at 540°F.

Case I/Case II comparison:

One m_C stream at 540°F (II) vs. two m_C at 300°F (I)

$$A = \infty(\text{II}) \text{ vs. } 2A(\text{I})$$

$$\Delta S(\text{II}) < \Delta S(\text{I})$$

Thus, for Case II, stream m_{CD} can heat, for example, another fluid to 520°F while stream m_{CA} and/or m_{CB} for Case I cannot.

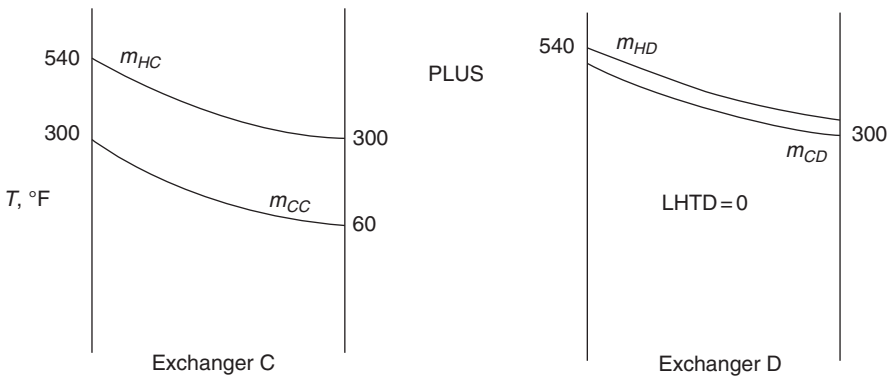


Figure 21.4 Heat exchanger comparison; Case II.

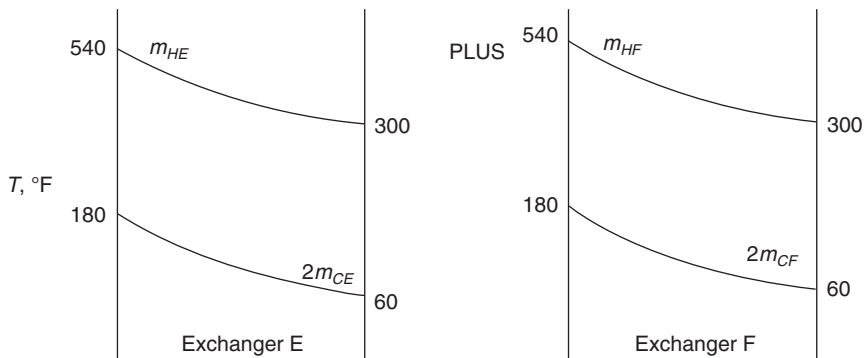


Figure 21.5 Heat exchanger comparison; Case III.

Consider Case III (see Figure 21.5). Here twice the coolant is employed in each exchanger. For Case III, one notes that:

LMTD has increased.

A has decreased.

ΔS has increased.

Also,

$$\text{LMTD}_F = \text{LMTD}_E > \text{LMTD}_C = \text{LMTD}_A = \text{LMTD}_B$$

$$A_F = A_E < A_A = A_B = A_C$$

$$\Delta S_F = \Delta S_E > \Delta S_A = \Delta S_B = \Delta S_C$$

End result: Four m_C at 180°F , A has decreased and ΔS has increased.

APPLICATIONS

The above analysis is extended to the four examples that follow.

ILLUSTRATIVE EXAMPLE 21.1

Refer to Case I, Figure 21.3, above. Calculate the entropy change of the two exchangers. For the purposes of analysis, arbitrarily assume $c_p = 1.0 \text{ Btu/lb} \cdot ^\circ\text{F}$ and $m_H = m_C = 1.0 \text{ lb}$.

SOLUTION: For the hot fluid,

$$\begin{aligned} \Delta S_H &= mc_p \ln \left(\frac{300 + 460}{540 + 460} \right) \\ &= (1)(1)(-0.2744) \\ &= -0.2744 \text{ Btu}/^\circ\text{F} \end{aligned}$$

For the cold fluid,

$$\begin{aligned}\Delta S_C &= mc_p \ln\left(\frac{300 + 460}{60 + 460}\right) \\ &= (1)(1)(0.3795) \\ &= 0.3795 \text{ Btu}/^\circ\text{F}\end{aligned}$$

Therefore, for one exchanger, say A:

$$\begin{aligned}\Delta S_A &= \Delta S_H + \Delta S_C \\ &= -0.2744 + 0.3795 \\ &= 0.1051 \text{ Btu}/^\circ\text{F}\end{aligned}$$

Since there are two similar exchangers

$$\Delta S_A = \Delta S_B$$

and

$$\begin{aligned}\Delta S_{\text{tot},I} &= (2)(0.1051) \\ &= 0.2102 \text{ Btu}/^\circ\text{F}\end{aligned}$$

As expected, there is a positive entropy change. ■

ILLUSTRATIVE EXAMPLE 21.2

Refer to Case II, Figure 21.4. Calculate the entropy change of exchangers C and D.

SOLUTION: Consider exchanger C first.

$$\Delta S_C = \Delta S_{HC} + \Delta S_{CC}$$

This is given by the result in the previous example, that is,

$$\Delta S_C = 0.1051 \text{ Btu}/^\circ\text{F}$$

Consider exchanger D. Since the temperature difference driving force is zero, the operation is reversible. Therefore,

$$\Delta S_D = 0$$

The total entropy change is then

$$\begin{aligned}\Delta S_{\text{tot},II} &= \Delta S_C + \Delta S_D \\ &= 0.1051 + 0.0 \\ &= 0.1051 \text{ Btu}/^\circ\text{F}\end{aligned}$$

■

ILLUSTRATIVE EXAMPLE 21.3

Refer to Case III, Figure 21.5. Calculate the entropy change in exchangers E and F.

SOLUTION: Consider exchanger E,

$$\begin{aligned}\Delta S_E &= \Delta S_{HE} + \Delta S_{CE} \\ &= -0.2744 + (2)(1) \ln\left(\frac{180 + 460}{60 + 460}\right) \\ &= -0.2744 + 0.4153 \\ &= 0.1409 \text{ Btu}/^\circ\text{F}\end{aligned}$$

Since there are two similar exchangers,

$$\Delta S_E = \Delta S_F$$

and

$$\begin{aligned}\Delta S_{\text{tot,III}} &= \Delta S_E + \Delta S_F \\ &= (2)(0.1409) \\ &= 0.2818 \text{ Btu}/^\circ\text{F}\end{aligned}$$

■

ILLUSTRATIVE EXAMPLE 21.4

Comment on the results of Illustrative Examples 21.1, 21.2, and 21.3.

SOLUTION: The calculated results of the three cases again paint a clear picture. As the LMTD decreases, the area cost requirement (per ft² of heat exchanger area) increases. In addition, the entropy change decreases, and the “quality” energy increases. Thus, from a “conservation of energy” perspective, second law considerations mandate its inclusion in heat exchanger applications with appropriate economic considerations; i.e., both the cost of the exchanger and the economic factors associated with the “quality” of the recovered energy must be considered in the analysis. Note that pressure drop, materials of construction, etc., are not included in this analysis.

The inclusion of economics in the analysis presented in Illustrative Examples 21.1–21.4 is treated in Chapter 27. The interested reader is encouraged to review Illustrative Example 27.12. ■

ILLUSTRATIVE EXAMPLE 21.5

Briefly discuss the use of interconnected networks of heat exchangers.

SOLUTION: Highly interconnected networks of exchangers can save a great deal of energy in a chemical plant. The more interconnected they are, however, the harder the plant is to operate, control, start-up, and shut-down. Often, auxiliary heat and cooling sources must be included in the plant design in order to ensure that the plant can operate smoothly. An excellent illustrative example is provided by Theodore et al.⁽⁴⁾ in Illustrative Example 28.11 in Chapter 28, Part Four. ■

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