

Chapter 5

The Second Law of Thermodynamics

Thermodynamics is concerned with transformations of energy, and the laws of thermodynamics describe the bounds within which these transformations are observed to occur. The first law reflects the observation that energy is conserved, but it imposes no restriction on the process direction. Yet, all experience indicates the existence of such a restriction, the concise statement of which constitutes the *second* law.

The differences between the two forms of energy, heat and work, provide some insight into the second law. In an energy balance, both work and heat are included as simple additive terms, implying that one unit of heat, a joule, is equivalent to the same unit of work. Although this is true with respect to an energy balance, experience teaches that there is a difference of kind between heat and work. This experience is summarized by the following facts.

Work is readily transformed into other forms of energy: for example, into potential energy by elevation of a weight, into kinetic energy by acceleration of a mass, into electrical energy by operation of a generator. These processes can be made to approach a conversion efficiency of 100% by elimination of friction, a dissipative process that transforms work into heat. Indeed, work is readily transformed completely into heat, as demonstrated by Joule's experiments.

On the other hand, all efforts to devise a process for the continuous conversion of heat completely into work or into mechanical or electrical energy have failed. Regardless of improvements to the devices employed, conversion efficiencies do not exceed about 40%. Evidently, heat is a form of energy intrinsically less useful and hence less valuable than an equal quantity of work or mechanical or electrical energy.

Drawing further on our experience, we know that the flow of heat between two bodies always takes place from the hotter to the cooler body, and never in the reverse direction. This fact is of such significance that its restatement serves as an acceptable expression of the second law.

5.1 STATEMENTS OF THE SECOND LAW

The observations just described suggest a general restriction on processes beyond that imposed by the first law. The second law is equally well expressed in two statements that describe this restriction:

- **Statement 1:** No apparatus can operate in such a way that its *only effect* (in system and surroundings) is to convert heat absorbed by a system *completely* into work done by the system.
- **Statement 2:** No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

Statement 1 does not say that heat cannot be converted into work; only that the process cannot leave both the system and its surroundings unchanged. Consider a system consisting of an ideal gas in a piston/cylinder assembly expanding reversibly at constant temperature. According to Eq. (2.3), $\Delta U^t = Q + W$. For an ideal gas, $\Delta U^t = 0$, and therefore, $Q = -W$. The heat absorbed by the gas from the surroundings is equal to the work transferred to the surroundings by the reversible expansion of the gas. At first this might seem a contradiction of statement 1, since in the surroundings the result is the complete conversion of heat into work. However, this statement requires in addition that no change occur in the system, a requirement that is not met.

This process is limited in another way, because the pressure of the gas soon reaches that of the surroundings, and expansion ceases. Therefore, the continuous production of work from heat by this method is impossible. If the original state of the system is restored in order to comply with the requirements of statement 1, energy from the surroundings in the form of work is needed to compress the gas back to its original pressure. At the same time energy as heat is transferred to the surroundings to maintain constant temperature. This reverse process requires at least the amount of work gained from the expansion; hence no net work is produced. Evidently, statement 1 may be expressed in an alternative way, *viz.*:

- **Statement 1a:** It is impossible by a cyclic process to convert the heat absorbed by a system completely into work done by the system.

The word *cyclic* requires that the system be restored periodically to its original state. In the case of a gas in a piston/cylinder assembly, its initial expansion and recompression to the original state constitute a complete cycle. If the process is repeated, it becomes a cyclic process. The restriction to a *cyclic* process in statement 1a amounts to the same limitation as that introduced by the words *only effect* in statement 1.

The second law does not prohibit the production of work from heat, but it does place a limit on how much of the heat directed into a cyclic process can be converted into work done by the process. With the exception of water and wind power, the partial conversion of heat into work is the basis for nearly all commercial production of power. The development of a quantitative expression for the efficiency of this conversion is the next step in the treatment of the second law.

5.2 HEAT ENGINES

The classical approach to the second law is based on a *macroscopic* viewpoint of properties, independent of any knowledge of the structure of matter or behavior of molecules. It arose from the study of *heat engines*, devices or machines that produce work from heat in a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically returns to its original state. In such a power plant the cycle (in its simplest form) consists of the following steps:

- Liquid water at ambient temperature is pumped into a boiler at high pressure.
- Heat from a fuel (heat of combustion of a fossil fuel or heat from a nuclear reaction) is transferred in the boiler to the water, converting it to high-temperature steam at the boiler pressure.
- Energy is transferred as shaft work from the steam to the surroundings by a device such as a turbine, in which the steam expands to reduced pressure and temperature.
- Exhaust steam from the turbine is condensed by transfer of heat to the surroundings, producing liquid water for return to the boiler, thus completing the cycle.

Essential to all heat-engine cycles are absorption of heat into the system at a high temperature, rejection of heat to the surroundings at a lower temperature, and production of work. In the theoretical treatment of heat engines, the two temperature levels which characterize their operation are maintained by *heat reservoirs*, bodies imagined capable of absorbing or rejecting an infinite quantity of heat without temperature change. In operation, the working fluid of a heat engine absorbs heat $|Q_H|$ from a hot reservoir, produces a net amount of work $|W|$, discards heat $|Q_C|$ to a cold reservoir, and returns to its initial state. The first law therefore reduces to:

$$|W| = |Q_H| - |Q_C| \quad (5.1)$$

The *thermal efficiency* of the engine is defined as:

$$\eta \equiv \frac{\text{net work output}}{\text{heat absorbed}}$$

With Eq. (5.1) this becomes:

$$\eta \equiv \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|}$$

or

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \quad (5.2)$$

Absolute-value signs are used to make the equations independent of the sign conventions for Q and W . For η to be unity (100% thermal efficiency), $|Q_C|$ must be zero. No engine has ever been built for which this is true; some heat is always rejected to the cold reservoir. This result of engineering experience is the basis for statements 1 and *la* of the second law.

If a thermal efficiency of 100% is not possible for heat engines, what then determines the upper limit? One would certainly expect the thermal efficiency of a heat engine to depend on the degree of reversibility of its operation. Indeed, a heat engine operating in a completely reversible manner is very special, and is called a *Carnot engine*. The characteristics of such an ideal engine were first described by N. L. S. Carnot¹ in 1824. The four steps that make up a *Carnot cycle* are performed in the following order:

- **Step 1:** A system at the temperature of a cold reservoir T_C undergoes a *reversible* adiabatic process that causes its temperature to rise to that of a hot reservoir at T_H .
- **Step 2:** The system maintains contact with the hot reservoir at T_H , and undergoes a *reversible* isothermal process during which heat $|Q_H|$ is absorbed from the hot reservoir.

¹Nicolas Leonard Sadi Carnot (1796–1832), a French engineer.

- **Step 3:** The system undergoes a *reversible* adiabatic process in the opposite direction of step 1 that brings its temperature back to that of the cold reservoir at T_C .
- **Step 4:** The system maintains contact with the reservoir at T_C , and undergoes a *reversible* isothermal process in the opposite direction of step 2 that returns it to its initial state with rejection of heat $|Q_C|$ to the cold reservoir.

A Carnot engine operates between two heat reservoirs in such a way that all heat absorbed is absorbed at the constant temperature of the hot reservoir and all heat rejected is rejected at the constant temperature of the cold reservoir. Any *reversible* engine operating between two heat reservoirs is a Carnot engine; an engine operating on a different cycle must necessarily transfer heat across finite temperature differences and therefore cannot be reversible.

Carnot's Theorem

Statement 2 of the second law is the basis for *Carnot's theorem*:

For two given heat reservoirs no engine can have a thermal efficiency higher than that of a Carnot engine.

To prove Carnot's theorem assume the existence of an engine E with a thermal efficiency *greater than* that of a Carnot engine which absorbs heat $|Q_H|$ from the hot reservoir, produces work $|W|$, and discards heat $|Q_H| - |W|$ to the cold reservoir. Engine E absorbs heat $|Q'_H|$ from the same hot reservoir, produces the same work $|W|$, and discards heat $|Q'_H| - |W|$ to the same cold reservoir. If engine E has the greater efficiency,

$$\frac{|W|}{|Q'_H|} > \frac{|W|}{|Q_H|} \quad \text{and} \quad |Q_H| > |Q'_H|$$

Since a Carnot engine is reversible, it may be operated in reverse; the Carnot cycle is then traversed in the opposite direction, and it becomes a reversible refrigeration cycle for which the quantities $|Q_H|$, $|Q_C|$, and $|W|$ are the same as for the engine cycle but are reversed in direction. Let engine E drive the Carnot engine backward as a Carnot refrigerator, as shown schematically in Fig. 5.1. For the engine/refrigerator combination, the net heat extracted from the cold reservoir is:

$$|Q_H| - |W| - (|Q'_H| - |W|) = |Q_H| - |Q'_H|$$

The net heat delivered to the hot reservoir is also $|Q_H| - |Q'_H|$. Thus, the sole result of the engine/refrigerator combination is the transfer of heat from temperature T_C to the higher temperature T_H . Since this is in violation of statement 2 of the second law, the original premise that engine E has a greater thermal efficiency than the Carnot engine is false, and Carnot's theorem is proved. In similar fashion, one can prove that all Carnot engines operating between heat reservoirs at the same two temperatures have the same thermal efficiency. Thus a *corollary to Carnot's theorem* states:

The thermal efficiency of a Carnot engine depends only on the temperature levels and not upon the working substance of the engine.

5.3 THERMODYNAMIC TEMPERATURE SCALES

In the preceding discussion we identified temperature levels by the kelvin scale, established with ideal-gas thermometry. This does not preclude taking advantage of the opportunity provided by the Carnot engine to establish a *thermodynamic* temperature scale that is truly independent

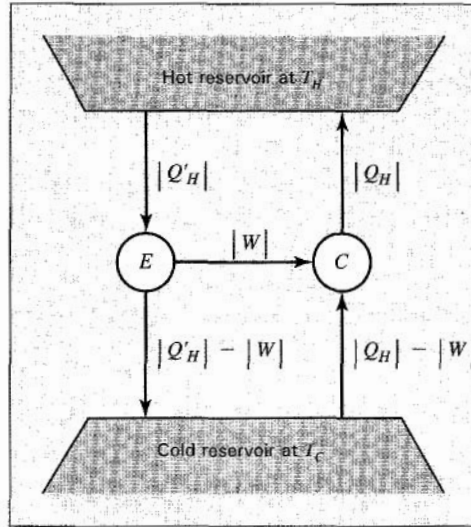


Figure 5.1 Engine E operating a Carnot refrigerator C

of any material properties. Let θ represent temperature on some empirical scale that unequivocally identifies temperature levels. Consider two Carnot engines, one operating between a hot reservoir at temperature θ_H and a cold reservoir at temperature θ_C , and a second operating between the reservoir at θ_C and a still colder reservoir at θ_F , as shown in Fig. 5.2. The heat rejected by the first engine $|Q_C|$ is absorbed by the second; therefore the two engines working together constitute a third Carnot engine absorbing heat $|Q_H|$ from the reservoir at θ_H and rejecting heat $|Q_F|$ to the reservoir at θ_F . The corollary to Carnot's theorem indicates that the thermal efficiency of the first engine is a function of θ_H and θ_C :

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} = \phi(\theta_H, \theta_C)$$

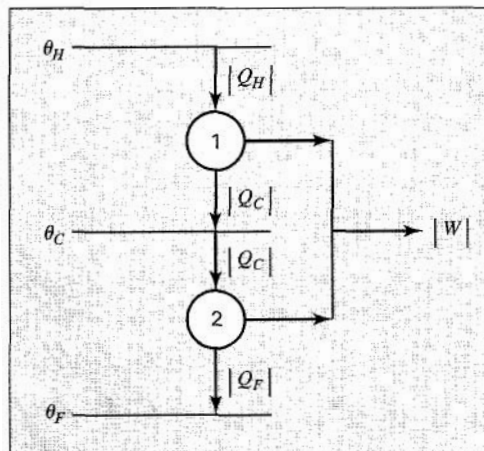


Figure 5.2 Carnot engines 1 and 2 constitute a third Carnot engine

Rearrangement gives:

$$\frac{|Q_H|}{|Q_C|} = \frac{1}{1 - \phi(\theta_H, \theta_C)} = f(\theta_H, \theta_C) \quad (5.3)$$

where f is an unknown function.

For the second and third engines, equations of the same functional form apply:

$$\frac{|Q_C|}{|Q_F|} = f(\theta_C, \theta_F) \quad \text{and} \quad \frac{|Q_H|}{|Q_F|} = f(\theta_H, \theta_F)$$

Division of the second of these equations by the first gives:

$$\frac{|Q_H|}{|Q_C|} = \frac{f(\theta_H, \theta_F)}{f(\theta_C, \theta_F)}$$

Comparison of this equation with Eq. (5.3) shows that the arbitrary temperature θ_F must cancel from the ratio on the right:

$$\frac{|Q_H|}{|Q_C|} = \frac{\psi(\theta_H)}{\psi(\theta_C)} \quad (5.4)$$

where ψ is another unknown function.

The right side of Eq. (5.4) is the ratio of ψ 's evaluated at two thermodynamic temperatures; the ψ 's are to each other as the absolute values of the heats absorbed and rejected by a Carnot engine operating between reservoirs at these temperatures, quite independent of the properties of any substance. Moreover, Eq. (5.4) allows arbitrary choice of the empirical temperature represented by 0; once this choice is made, the function ψ must be determined. If 0 is chosen as the kelvin temperature T , then Eq. (5.4) becomes:

$$\frac{|Q_H|}{|Q_C|} = \frac{\psi(T_H)}{\psi(T_C)} \quad (5.5)$$

Ideal-Gas Temperature Scale; Carnot's Equations

The cycle traversed by an ideal gas serving as the working fluid in a Carnot engine is shown by a PV diagram in Fig. 5.3. It consists of four *reversible* steps:

- $a \rightarrow b$ Adiabatic compression until the temperature rises from T_C to T_H .
- $b \rightarrow c$ Isothermal expansion to arbitrary point c with absorption of heat $|Q_H|$.
- $c \rightarrow d$ Adiabatic expansion until the temperature decreases to T_C .
- $d \rightarrow a$ Isothermal compression to the initial state with rejection of heat $|Q_C|$.

For the isothermal steps $b \rightarrow c$ and $d \rightarrow a$, Eq. (3.26) yields:

$$|Q_H| = RT_H \ln \frac{V_c}{V_b} \quad \text{and} \quad |Q_C| = RT_C \ln \frac{V_d}{V_a}$$

Therefore,

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H \ln(V_c/V_b)}{T_C \ln(V_d/V_a)} \quad (5.6)$$

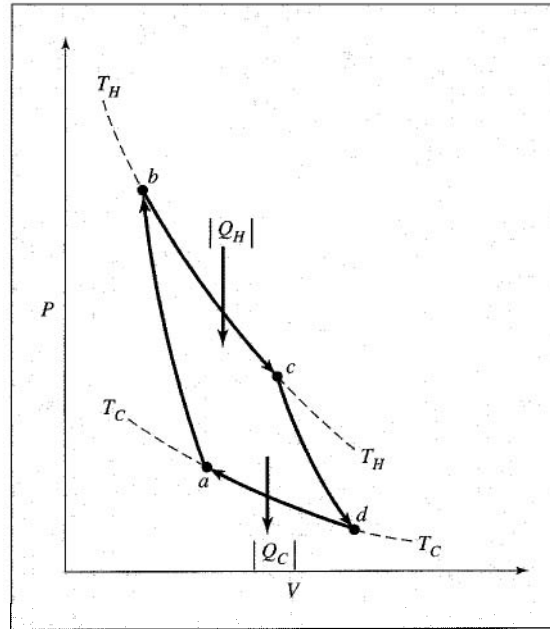


Figure 5.3 PV diagram showing Carnot cycle for an ideal gas

For an adiabatic process Eq. (3.21) is written,

$$-\frac{C_V}{R} \frac{dT}{T} = \frac{dV}{V}$$

For step $a \rightarrow b$ and $c \rightarrow d$, integration gives:

$$\int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln \frac{V_a}{V_b} \quad \text{and} \quad \int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = \ln \frac{V_d}{V_c}$$

Since the left sides of these two equations are the same,

$$\ln \frac{V_a}{V_b} = \ln \frac{V_d}{V_c} \quad \text{or} \quad \ln \frac{V_c}{V_b} = \ln \frac{V_d}{V_a}$$

Equation (5.6) now becomes:

$$\boxed{\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C}} \quad (5.7)$$

Comparison of this result with Eq. (5.5) yields the simplest possible functional relation for ψ , namely, $\psi(T) = T$. We conclude that the kelvin temperature scale, based on the properties of ideal gases, is in fact a thermodynamic scale, independent of the characteristics of any particular substance. Substitution of Eq. (5.7) into Eq. (5.2) gives:

$$\boxed{\eta \equiv \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}} \quad (5.8)$$

Equations (5.7) and (5.8) are known as *Carnot's equations*. In Eq. (5.7) the smallest possible value of $|Q_C|$ is zero; the corresponding value of T_C is the absolute zero of temperature on the kelvinscale. As mentioned in Sec. 1.5, this occurs at (-273.15°C) . Equation (5.8) shows that the thermal efficiency of a Carnot engine can approach unity only when T_H approaches infinity or T_C approaches zero. Neither of these conditions is attainable; all heat engines therefore operate with thermal efficiencies less than unity. The cold reservoirs naturally available on earth are the atmosphere, lakes and rivers, and the oceans, for which $T_C \simeq 300\text{ K}$. Hot reservoirs are objects such as furnaces where the temperature is maintained by combustion of fossil fuels and nuclear reactors where the temperature is maintained by fission of radioactive elements. For these practical heat sources, $T_H \simeq 600\text{ K}$. With these values,

$$\eta = 1 - \frac{300}{600} = 0.5$$

This is a rough practical limit for the thermal efficiency of a Carnot engine; actual heat engines are irreversible, and their thermal efficiencies rarely exceed 0.35.

Example 5.1

A central power plant, rated at 800 000 kW, generates steam at 585 K and discards heat to a river at 295 K. If the thermal efficiency of the plant is 70% of the maximum possible value, how much heat is discarded to the river at rated power?

Solution 5.1

The maximum possible thermal efficiency is given by Eq. (5.8). With T_H as the steam-generation temperature and T_C as the river temperature:

$$\eta_{\max} = 1 - \frac{295}{585} = 0.4957 \quad \text{and} \quad \eta = (0.7)(0.4957) = 0.3470$$

where η is the actual thermal efficiency. Equations (5.1) and (5.2) may be combined to eliminate $|Q_H|$; solution for $|Q_C|$ then yields:

$$\begin{aligned} |Q_C| &= \left(\frac{1-\eta}{\eta} \right) |W| \\ &= \left(\frac{1-0.347}{0.347} \right) (800\,000) = 1\,505\,500\text{ kW} \end{aligned}$$

This amount of heat would raise the temperature of a moderate-size river several degrees Celsius.

5.4 ENTROPY

Equation (5.7) for a Carnot engine may be written:

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}$$

If the heat quantities refer to the engine (rather than to the heat reservoirs), the numerical value of Q_H is positive and that of Q_C is negative. The equivalent equation written without absolute-value signs is therefore

$$\frac{Q_H}{T_H} = \frac{-Q_C}{T_C}$$

or

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \quad (5.9)$$

Thus for a complete cycle of a Carnot engine, the two quantities Q/T associated with the absorption and rejection of heat by the working fluid of the engine sum to zero. The working fluid of a cyclic engine periodically returns to its initial state, and its properties, e.g., temperature, pressure, and internal energy, return to their initial values. Indeed, a primary characteristic of a property is that the sum of its changes is zero for any complete cycle. Thus for a Carnot cycle Eq. (5.9) suggests the existence of a property whose changes are given by the quantities Q/T .

Our purpose now is to show that Eq. (5.9), applicable to the reversible Carnot cycle, also applies to other reversible cycles. The closed curve on the PV diagram of Fig. 5.4 represents an arbitrary reversible cycle traversed by an arbitrary fluid. Divide the enclosed area by a series of reversible adiabatic curves; since such curves cannot intersect (Pb. 5.1), they may be drawn arbitrarily close to one another. Several such curves are shown on the figure as long dashed lines. Connect adjacent adiabatic curves by two short reversible isotherms which approximate the curve of the arbitrary cycle as closely as possible. The approximation clearly improves as the adiabatic curves are more closely spaced. When the separation becomes arbitrarily small, the original cycle is faithfully represented. Each pair of adjacent adiabatic curves and their isothermal connecting curves represent a Carnot cycle for which Eq. (5.9) applies.

Each Carnot cycle has its own pair of isotherms T_H and T_C and associated heat quantities Q_H and Q_C . These are indicated on Fig. 5.4 for a representative cycle. When the adiabatic curves are so closely spaced that the isothermal steps are infinitesimal, the heat quantities become dQ_H and dQ_C , and Eq. (5.9) for each Carnot cycle is written:

$$\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = 0$$

In this equation T_H and T_C , absolute temperatures of the working fluid of the Carnot engines, are also the temperatures traversed by the working fluid of the arbitrary cycle. Summation of all quantities dQ/T for the Carnot engines leads to the integral:

$$\oint \frac{dQ_{\text{rev}}}{T} = 0 \quad (5.10)$$

where the circle in the integral sign signifies integration over the arbitrary cycle, and the subscript "rev" indicates that the cycle is reversible.

Thus the quantities dQ_{rev}/T sum to zero for the arbitrary cycle, exhibiting the characteristic of a property. We therefore infer the existence of a property whose differential changes for the arbitrary cycle are given by these quantities. The property is called *entropy* (en'-tro-py), and its differential changes are:

$$dS' = \frac{dQ_{\text{rev}}}{T} \quad (5.11)$$

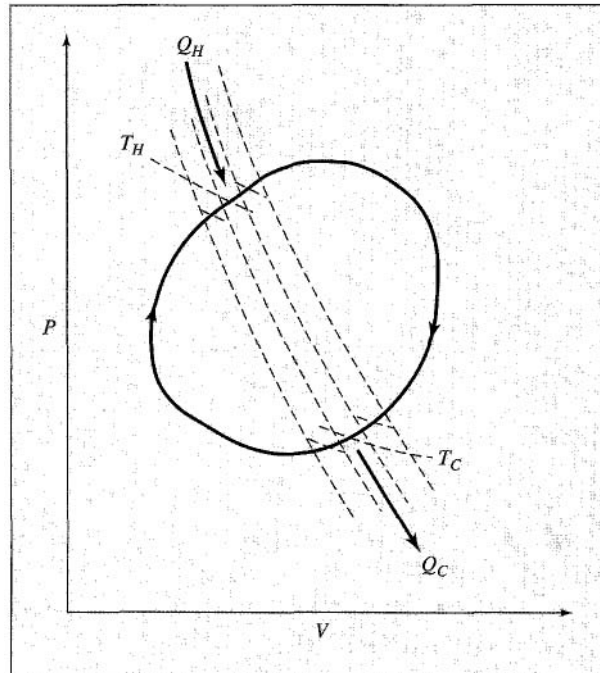


Figure 5.4 An arbitrary reversible cyclic process drawn on a PV diagram

where S^t is the total (rather than molar) entropy of the system. Alternatively,

$$\boxed{dQ_{\text{rev}} = T dS^t} \quad (5.12)$$

Points A and B on the PV diagram of Fig. 5.5 represent two equilibrium states of a particular fluid, and paths ACB and ADB show two arbitrary reversible processes connecting these points. Integration of Eq. (5.11) for each path gives:

$$\Delta S^t = \int_{ACB} \frac{dQ_{\text{rev}}}{T} \quad \text{and} \quad = \int_{ADB} \frac{dQ_{\text{rev}}}{T}$$

where in view of Eq. (5.10) the two integrals must be equal. We therefore conclude that ΔS^t is independent of path and is a property change given by $S_B^t - S_A^t$.

If the fluid is changed from state A to state B by an *irreversible* process, the entropy change must still be $\Delta S^t = S_B^t - S_A^t$, but experiment shows that this result is *not* given by $\int dQ/T$ evaluated for the irreversible process itself, because the calculation of entropy changes by this integral must in general be along reversible paths.

The entropy change of a *heat reservoir*, however, is always given by Q/T , where Q is the quantity of heat transferred to or from the reservoir at temperature T , whether the transfer is reversible or irreversible. The reason is that the effect of heat transfer on a heat reservoir is the same regardless of the temperature of the source or sink of the heat.

If a process is reversible and adiabatic, $dQ_{\text{rev}} = 0$; then by Eq. (5.11), $dS^t = 0$. Thus the entropy of a system is constant during a reversible adiabatic process, and the process is said to be *isentropic*.

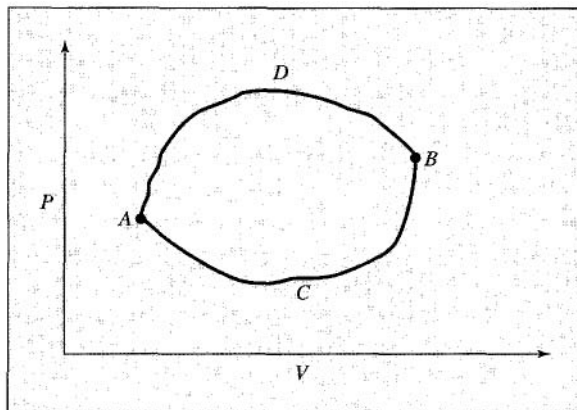


Figure 5.5 Two reversible paths joining equilibrium states A and B

This discussion of entropy can be summarized as follows:

- Entropy owes its existence to the second law, from which it arises in much the same way as internal energy does from the first law. Equation (5.11) is the ultimate source of all equations that relate the entropy to measurable quantities. It does not represent a definition of entropy; there is none in the context of classical thermodynamics. What it provides is the means for calculating *changes* in this property. Its essential nature is summarized by the following axiom:

There exists a property called entropy S , which is an intrinsic property of a system, functionally related to the measurable coordinates which characterize the system. For a reversible process, changes in this property are given by Eq. (5.11).

- The change in entropy of any system undergoing a finite *reversible* process is:

$$\Delta S^t = \int \frac{dQ_{\text{rev}}}{T} \quad (5.13)$$

- When a system undergoes an *irreversible* process between two equilibrium states, the entropy change of the system ΔS^t is evaluated by application of Eq. (5.13) to an *arbitrarily chosen reversible process* that accomplishes the same change of state as the actual process. Integration is *not* carried out for the irreversible path. Since entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.

In the special case of a *mechanically reversible* process (Sec. 2.8), the entropy change of the system is correctly evaluated from $\int dQ/T$ applied to the actual process, even though the *heat transfer* between system and surroundings is irreversible. The reason is that it is immaterial, as far as the system is concerned, whether the temperature difference causing the heat transfer is differential (making the process reversible) or finite. The entropy change of a system *caused by the transfer of heat* can always be calculated by $\int dQ/T$, whether the heat transfer is accomplished reversibly or irreversibly. However, when a process is irreversible on account of finite differences in other driving forces, such as pressure, the entropy change is not caused solely by the heat transfer, and for its calculation one must devise a reversible means of accomplishing the same change of state.

This introduction to entropy through a consideration of heat engines is the classical approach, closely following its actual historical development. A complementary approach, based on molecular concepts and statistical mechanics, is considered briefly in Sec. 5.11.

5.5 ENTROPY CHANGES OF AN IDEAL GAS

For one mole or a unit mass of fluid undergoing a mechanically reversible process in a closed system, the first law, Eq. (2.8), becomes:

$$dU = dQ_{\text{rev}} - P dV$$

Differentiation of the defining equation for enthalpy, $H = U + PV$, yields:

$$dH = dU + P dV + V dP$$

Eliminating dU gives:

$$dH = dQ_{\text{rev}} - P dV + P dV + V dP$$

or

$$dQ_{\text{rev}} = dH - V dP$$

For an ideal gas, $dH = C_P^{\text{ig}} dT$ and $V = RT/P$. With these substitutions and then division by T ,

$$\frac{dQ_{\text{rev}}}{T} = C_P^{\text{ig}} \frac{dT}{T} - R \frac{dP}{P}$$

As a result of Eq. (5.11), this becomes:

$$dS = C_P^{\text{ig}} \frac{dT}{T} - R \frac{dP}{P} \quad \text{or} \quad \frac{dS}{R} = \frac{C_P^{\text{ig}}}{R} \frac{dT}{T} - d \ln P$$

where S is the molar entropy of an ideal gas. Integration from an initial state at conditions T_0 and P_0 to a final state at conditions T and P gives:

$$\boxed{\frac{\Delta S}{R} = \int_{T_0}^T \frac{C_P^{\text{ig}}}{R} \frac{dT}{T} - \ln \frac{P}{P_0}} \quad (5.14)$$

Although *derived* for a mechanically reversible process, this equation relates properties only, and is independent of the process causing the change of state. It is therefore a general equation for the calculation of entropy changes of an ideal gas.

Example 5.2

For an ideal gas with constant heat capacities undergoing a reversible adiabatic (and therefore isentropic) process, Eq. (3.29b) can be written:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma}$$

Show that this same equation results from application of Eq. (5.14) with $\Delta S = 0$.

Solution 5.2

Since C_p^{ig} is constant, Eq. (5.14) can be written:

$$0 = \ln \frac{T_2}{T_1} - \frac{R}{C_p^{ig}} \ln \frac{P_2}{P_1}$$

Whence,
$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{R/C_p^{ig}} \quad (A)$$

By Eq. (3.18) for an ideal gas,

$$C_p^{ig} = C_v^{ig} + R \quad \text{or} \quad 1 = \frac{C_v^{ig}}{C_p^{ig}} + \frac{R}{C_p^{ig}} = \frac{1}{\gamma} + \frac{R}{C_p^{ig}}$$

where $\gamma = C_p^{ig}/C_v^{ig}$. Solving for R/C_p^{ig} gives:

$$\frac{R}{C_p^{ig}} = \frac{\gamma - 1}{\gamma}$$

This transforms Eq. (A) into the given equation.

Equation (4.4) for the temperature dependence of the molar heat capacity C_p^{ig} allows integration of the first term on the right of Eq. (5.14). The result is conveniently expressed as

$$\int_{T_0}^T \frac{C_p^{ig}}{R} \frac{dT}{T} = A \ln \tau + \left[BT_0 + \left(CT_0^2 + \frac{D}{\tau^2 T_0^2} \right) \left(\frac{\tau + 1}{2} \right) \right] (\tau - 1) \quad (5.15)$$

where
$$\tau \equiv \frac{T}{T_0}$$

Since this integral must often be evaluated, we include in App. D representative computer programs for its evaluation. For computational purposes the right side of Eq. (5.15) is defined as the function, ICPS(T₀, T; A, B, C, D). Equation (5.15) then becomes:

$$\int_{T_0}^T \frac{C_p^{ig}}{R} \frac{dT}{T} = \text{ICPS}(T_0, T; A, B, C, D)$$

The computer programs also calculate a mean heat capacity defined as:

$$\langle C_p^{ig} \rangle_S = \frac{\int_{T_0}^T C_p^{ig} dT / T}{\ln(T/T_0)} \quad (5.16)$$

Here, the subscript "S" denotes a mean value specific to entropy calculations. Division of Eq. (5.15) by $\ln(T/T_0)$ or $\ln \tau$ therefore yields:

$$\frac{\langle C_p^{ig} \rangle_S}{R} = A + \left[BT_0 + \left(CT_0^2 + \frac{D}{\tau^2 T_0^2} \right) \left(\frac{\tau + 1}{2} \right) \right] \left(\frac{\tau - 1}{\ln \tau} \right) \quad (5.17)$$

The right side of this equation is defined as another function, $\text{MCPS}(T_0, T; A, B, C, D)$. Equation (5.17) then becomes:

$$\frac{\langle C_P^{ig} \rangle_S}{R} = \text{MCPS}(T_0, T; A, B, C, D)$$

Solving for the integral in Eq. (5.16) gives:

$$\int_{T_0}^T C_P^{ig} \frac{dT}{T} = \langle C_P^{ig} \rangle_S \ln \frac{T}{T_0}$$

and Eq. (5.14) becomes:

$$\boxed{\frac{\Delta S}{R} = \frac{\langle C_P^{ig} \rangle_S}{R} \ln \frac{T}{T_0} - \ln \frac{P}{P_0}} \quad (5.18)$$

This form of the equation for entropy changes of an ideal gas may be useful when iterative calculations are required.

Example 5.3

Methane gas at 550 K and 5 bar undergoes a reversible adiabatic expansion to 1 bar. Assuming methane to be an ideal gas at these conditions, determine its final temperature.

Solution 5.3

For this process $\Delta S = 0$, and Eq. (5.18) becomes:

$$\frac{\langle C_P^{ig} \rangle_S}{R} \ln \frac{T_2}{T_1} = \ln \frac{P_2}{P_1} = \ln \frac{1}{5} = -1.6094$$

Since $\langle C_P^{ig} \rangle_S$ depends on T_2 , we rearrange this equation for iterative solution:

$$\ln \frac{T_2}{T_1} = \frac{-1.6094}{\langle C_P^{ig} \rangle_S / R}$$

Whence,
$$T_2 = T_1 \exp\left(\frac{-1.6094}{\langle C_P^{ig} \rangle_S / R}\right) \quad (A)$$

Evaluation of $\langle C_P^{ig} \rangle_S / R$ is by Eq. (5.17) with constants from Table C.1. Functionally,

$$\frac{\langle C_P^{ig} \rangle_S}{R} = \text{MCPS}(550, T_2; 1.702, 9.081E-3, -2.164E-6, 0.0)$$

With an initial value of $T_2 < 550$, compute a value of $\langle C_P^{ig} \rangle_S / R$ for substitution into Eq. (A). This yields a new value of T_2 from which to recompute $\langle C_P^{ig} \rangle_S / R$, and the process continues to convergence on a final value of $T_2 = 411.34$ K.

5.6 MATHEMATICAL STATEMENT OF THE SECOND LAW

Consider two heat reservoirs, one at temperature T_H and a second at the lower temperature T_C . Let a quantity of heat $|Q|$ be transferred from the hotter to the cooler reservoir. The entropy changes of the reservoirs at T_H and at T_C are:

$$\Delta S_H^t = \frac{-|Q|}{T_H} \quad \text{and} \quad \Delta S_C^t = \frac{|Q|}{T_C}$$

These two entropy changes are added to give:

$$\Delta S_{\text{total}} = \Delta S_H^t + \Delta S_C^t = \frac{-|Q|}{T_H} + \frac{|Q|}{T_C} = |Q| \left(\frac{T_H - T_C}{T_H T_C} \right)$$

Since $T_H > T_C$, the total entropy change as a result of this irreversible process is positive. Also, ΔS_{total} becomes smaller as the difference $T_H - T_C$ gets smaller. When T_H is only infinitesimally higher than T_C , the heat transfer is reversible, and ΔS_{total} approaches zero. Thus for the process of irreversible heat transfer, ΔS_{total} is always positive, approaching zero as the process becomes reversible.

Consider now an irreversible process in a closed system wherein no heat transfer occurs. Such a process is represented on the P V diagram of Fig. 5.6, which shows an irreversible, adiabatic expansion of 1 mol of fluid from an initial equilibrium state at point A to a final equilibrium state at point B. Now suppose the fluid is restored to its initial state by a reversible process consisting of two steps: first, the reversible, adiabatic (constant-entropy) compression of the fluid to the initial pressure, and second, a reversible, constant-pressure step that restores the initial volume. If the initial process results in an entropy change of the fluid, then there must be heat transfer during the reversible, constant-P second step such that:

$$\Delta S^t = S_A^t - S_B^t = \int_B^A \frac{dQ_{\text{rev}}}{T}$$

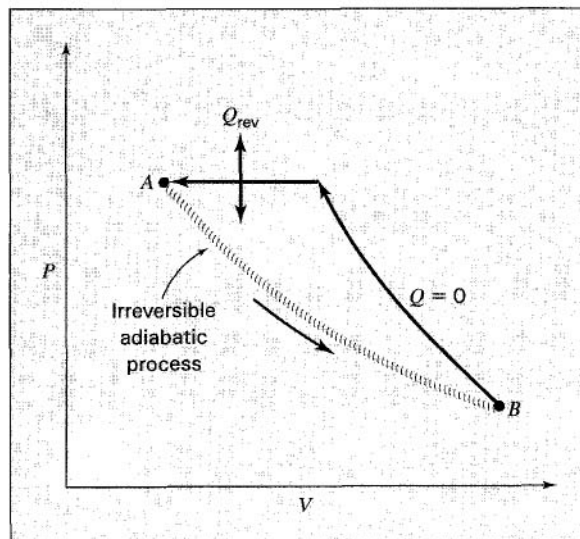


Figure 5.6 Cycle containing an irreversible adiabatic process A to B

The original irreversible process and the reversible restoration process constitute a cycle for which $\Delta U = 0$ and for which the work is therefore:

$$-W = Q_{\text{rev}} = \int_B^A dQ_{\text{rev}}$$

However, according to statement 1a of the second law, Q_{rev} cannot be directed *into* the system, for the cycle would then be a process for the complete conversion into work of the heat absorbed. Thus, $\int dQ_{\text{rev}}$ is negative, and it follows that $S_B^f - S_A^f$ is also negative; whence $S_B^f > S_A^f$. Since the original irreversible process is adiabatic ($\Delta S_{\text{total}} = 0$), the total entropy change of the system and surroundings as a result of the process is $\Delta S_{\text{total}} = S_B^f - S_A^f > 0$.

In arriving at this result, our presumption is that the original irreversible process results in an entropy change of the fluid. If the original process is in fact isentropic, then the system can be restored to its initial state by a simple reversible adiabatic process. This cycle is accomplished with no heat transfer and therefore with no net work. Thus the system is restored without leaving any change elsewhere, and this implies that the original process is reversible rather than irreversible.

Thus the same result is found for adiabatic processes as for direct heat transfer: ΔS_{total} is always positive, approaching zero as a limit when the process becomes reversible. This same conclusion can be demonstrated for any process whatever, leading to the general equation:

$$\boxed{\Delta S_{\text{total}} \geq 0} \quad (5.19)$$

This mathematical statement of the second law affirms that every process proceeds in such a direction that the *total* entropy change associated with it is positive, the limiting value of zero being attained only by a reversible process. No process is possible for which the total entropy decreases.

We return now to a cyclic heat engine that takes in heat $|Q_H|$ from a heat reservoir at T_H , and discards heat $|Q_C|$ to another heat reservoir at T_C . Since the engine operates in cycles, it undergoes no net changes in its properties. The total entropy change of the process is therefore the sum of the entropy changes of the heat reservoirs:

$$\Delta S_{\text{total}} = \frac{-|Q_H|}{T_H} + \frac{|Q_C|}{T_C}$$

The work produced by the engine is

$$|W| = |Q_H| - |Q_C| \quad (5.1)$$

Elimination of $|Q_C|$ between these two equations and solution for $|W|$ gives:

$$|W| = -T_C \Delta S_{\text{total}} + |Q_H| \left(1 - \frac{T_C}{T_H} \right)$$

This is the general equation for work of a heat engine for temperature levels T_C and T_H . The minimum work output is zero, resulting when the engine is completely inefficient and the process degenerates into simple irreversible heat transfer between the two heat reservoirs. In this case solution for ΔS_{total} yields the equation obtained at the beginning of this section. The maximum work is obtained when the engine is reversible, in which case $\Delta S_{\text{total}} = 0$, and the equation reduces to the second term on the right, the work of a Carnot engine.

Example 5.4

A 40-kg steel casting ($C_p = 0.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$) at a temperature of 723.15 K (450°C) is quenched in 150 kg of oil ($C_p = 2.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$) at 298.15 K (25°C). If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together?

Solution 5.4

The final temperature T of the oil and the steel casting is found by an energy balance. Since the change in energy of the oil and steel together must be zero,

$$(40)(0.5)(T - 723.15) + (150)(2.5)(T - 298.15) = 0$$

Solution yields $T = 319.67 \text{ K}$ or 46.52°C .

(a) Change in entropy of the casting:

$$\begin{aligned} \Delta S' &= \int \frac{dQ}{T} = m \int \frac{C_p dT}{T} = mC_p \ln \frac{T_2}{T_1} \\ &= (40)(0.5) \ln \frac{319.67}{723.15} = -16.33 \text{ kJ K}^{-1} \end{aligned}$$

(b) Change in entropy of the oil:

$$\Delta S' = (150)(2.5) \ln \frac{319.67}{298.15} = 26.13 \text{ kJ K}^{-1}$$

(c) Total entropy change:

$$\Delta S_{\text{total}} = -16.33 + 26.13 = 9.80 \text{ kJ K}^{-1}$$

Note that although the total entropy change is positive, the entropy of the casting has decreased.

5.7 ENTROPY BALANCE FOR OPEN SYSTEMS

Just as an energy balance can be written for processes in which fluid enters, exits, or flows through a control volume (Sec. 2.12), so too can an entropy balance be written. There is, however, an important difference: *Entropy is not conserved*. The second law states that the *total* entropy change associated with any process must be positive, with a limiting value of zero for a reversible process. This requirement is taken into account by writing the entropy balance for both the system and its surroundings, considered together, and by including an *entropy-generation* term to account for the irreversibilities of the process. This term is the sum of three others: one for entropy changes in the streams flowing in and out of the control volume, one for entropy changes within the control volume, and one for entropy changes in the surroundings. If the process is reversible, these three terms sum to zero so that $\Delta S_{\text{total}} = 0$. If the process is irreversible, they sum to a positive quantity, the entropy-generation term.

The statement of balance, expressed as rates, is therefore:

$$\left\{ \begin{array}{l} \text{Net rate of} \\ \text{change in} \\ \text{entropy of} \\ \text{flowing streams} \end{array} \right\} + \left\{ \begin{array}{l} \text{Time rate of} \\ \text{change of} \\ \text{entropy} \\ \text{in control} \\ \text{volume} \end{array} \right\} + \left\{ \begin{array}{l} \text{Time rate of} \\ \text{change of} \\ \text{entropy in} \\ \text{surroundings} \end{array} \right\} = \left\{ \begin{array}{l} \text{Total rate} \\ \text{of entropy} \\ \text{generation} \end{array} \right\}$$

The equivalent *equation of entropy balance* is

$$\Delta(\dot{m}S)_{fs} + \frac{d(mS)_{cv}}{dt} + \frac{dS'_{surr}}{dt} = \dot{S}_G \geq 0 \quad (5.20)$$

where \dot{S}_G is the rate of entropy generation. This equation is the general *rate* form of the entropy balance, applicable at any instant. Each term can vary with time. The first term is simply the net rate of gain in entropy of the flowing streams, i.e., the difference between the total entropy transported out by exit streams and the total entropy transported in by entrance streams. The second term is the time rate of change of the total entropy of the fluid contained within the control volume. The third term accounts for entropy changes in the surroundings, the result of heat transfer between system and surroundings.

Let rate of heat transfer \dot{Q}_j with respect to a particular part of the control surface be associated with $T_{\sigma,j}$ where subscript a, j denotes a temperature in the surroundings. The rate of entropy change in the surroundings as a result of this transfer is then $-\dot{Q}_j/T_{\sigma,j}$. The minus sign converts \dot{Q}_j , defined with respect to the system, to a heat rate with respect to the surroundings. The third term in Eq. (5.20) is therefore the sum of all such quantities:

$$\frac{dS'_{surr}}{dt} = - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}}$$

Equation (5.20) is now written:

$$\boxed{\Delta(\dot{m}S)_{fs} + \frac{d(mS)_{cv}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0} \quad (5.21)$$

The final term, representing the *rate of entropy generation* \dot{S}_G , reflects the second-law requirement that it be positive for irreversible processes. There are two sources of irreversibility: (a) those *within* the control volume, i.e., *internal* irreversibilities, and (b) those resulting from heat transfer across finite temperature differences between system and surroundings, i.e., *external* thermal irreversibilities. In the limiting case where $\dot{S}_G = 0$, the process must be *completely reversible*, implying:

- The process is internally reversible within the control volume.
- Heat transfer between the control volume and its surroundings is reversible.

The second item means either that heat reservoirs are included in the surroundings with temperatures equal to those of the control surface or that Carnot engines are interposed in the surroundings between the control-surface temperatures and the heat-reservoir temperatures.

For a steady-state flow process the mass and entropy of the fluid in the control volume are constant, and $d(mS)_{cv}/dt$ is zero. Equation (5.21) then becomes:

$$\Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \quad (5.22)$$

If in addition there is but one entrance and one exit, with m the same for both streams, dividing through by \dot{m} yields:

$$\Delta S - \sum_j \frac{Q_j}{T_{\sigma,j}} = S_G \geq 0 \quad (5.23)$$

Each term in Eq. (5.23) is based on a unit amount of fluid flowing through the control volume.

Example 5.5

In a steady-state flow process, 1 mol s^{-1} of air at 600 K and 1 atm is continuously mixed with 2 mol s^{-1} of air at 450 K and 1 atm. The product stream is at 400 K and 1 atm. A schematic representation of the process is shown in Fig. 5.7. Determine the rate of heat transfer and the rate of entropy generation for the process. Assume that air is an ideal gas with $C_P = (7/2)R$, that the surroundings are at 300 K, and that kinetic- and potential-energy changes are negligible.

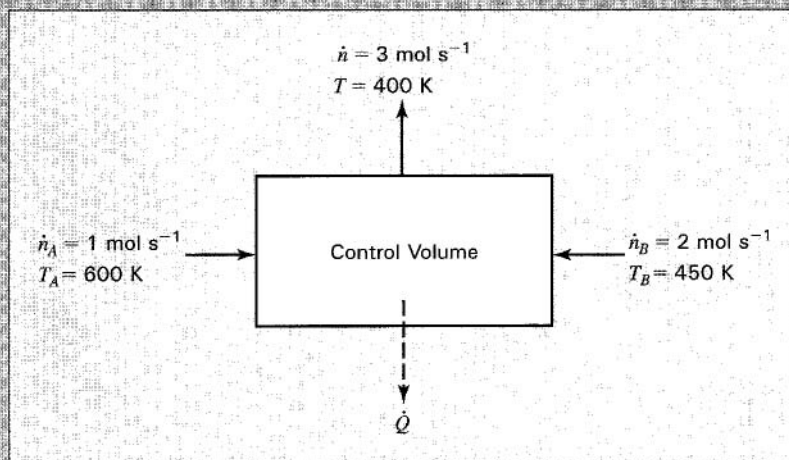


Figure 5.7 Process described in Ex. 5.5

Solution 5.5

By Eq. (2.30), with m replaced by \dot{n} ,

$$\begin{aligned} Q &= \dot{n}H - \dot{n}_A H_A - \dot{n}_B H_B = \dot{n}_A (H - H_A) + \dot{n}_B (H - H_B) \\ &= \dot{n}_A C_P (T - T_A) + \dot{n}_B C_P (T - T_B) = C_P [\dot{n}_A (T - T_A) + \dot{n}_B (T - T_B)] \\ &= (7/2)(8.314) [(1)(400 - 600) + (2)(400 - 450)] = -8729.7 \text{ J s}^{-1} \text{ or W} \end{aligned}$$

By Eq. (5.22), again with m replaced by \dot{n} ,

$$\begin{aligned}\dot{S}_G &= \dot{n}S - \dot{n}_A S_A - \dot{n}_B S_B - \frac{\dot{Q}}{T_\sigma} = \dot{n}_A(S - S_A) + \dot{n}_B(S - S_B) - \frac{\dot{Q}}{T_\sigma} \\ &= \dot{n}_A C_P \ln \frac{T}{T_A} + \dot{n}_B C_P \ln \frac{T}{T_B} - \frac{\dot{Q}}{T_\sigma} = C_P \left(\dot{n}_A \ln \frac{T}{T_A} + \dot{n}_B \ln \frac{T}{T_B} \right) - \frac{\dot{Q}}{T_\sigma} \\ &= (7/2)(8.314) \left[(1) \ln \frac{400}{600} + (2) \ln \frac{400}{450} \right] + \frac{8729.7}{300} = 10.446 \text{ J K}^{-1} \text{ s}^{-1}\end{aligned}$$

The rate of entropy generation is positive, as it must be for any real process.

Example 5.6

An inventor claims to have devised a process which takes in only saturated steam at 373.15 K (100°C) and which by a complicated series of steps makes heat continuously available at a temperature level of 473.15 K (200°C). The inventor claims further that, for every kilogram of steam taken into the process, 2000 kJ of energy as heat is liberated at the temperature level of 473.15 K (200°C). Show whether or not this process is possible. In order to give the inventor the benefit of any doubt, assume cooling water available in unlimited quantity at a temperature of 273.15 K (0°C).

Solution 5.6

For any process to be theoretically possible, it must meet the requirements of the first and second laws of thermodynamics. The detailed mechanism need not be known in order to determine whether this is the case; only the overall result is required. If the claims of the inventor satisfy the laws of thermodynamics, means for realizing the claims are theoretically possible. The determination of a mechanism is then a matter of ingenuity. Otherwise, the process is impossible, and no mechanism for carrying it out can be devised.

In the present instance, a continuous process takes in saturated steam, and heat is made continuously available at a temperature level $T' = 473.15 \text{ K}$ (200°C). Since cooling water is available at $T_\sigma = 273.15 \text{ K}$ (0°C), maximum use can be made of the steam by cooling it to this temperature. Assume therefore that the steam is condensed and cooled to 273.15 K (0°C) and is discharged from the process at this temperature and at atmospheric pressure. All the heat liberated in this operation cannot be made available at temperature level $T' = 473.15 \text{ K}$ (200°C), because this would violate statement 2 of the second law. We must suppose that some heat Q_σ is transferred to the cooling water at $T_\sigma = 273.15 \text{ K}$ (0°C). Moreover, the process must satisfy the first law; thus by Eq. (2.33):

$$\Delta H = Q + W_s$$

where ΔH is the enthalpy change of the steam as it flows through the apparatus and Q is the total heat transfer between the apparatus and its surroundings. Since no shaft work accompanies the process, $W_s = 0$. The surroundings consist of cooling water, which acts as a heat reservoir at the constant temperature of $T_\sigma =$

273.15 K (0°C), and a heat reservoir at $T' = 473.15$ K (200°C) to which heat in the amount of 2000 kJ is transferred for each kilogram of steam entering the apparatus. The diagram of Fig. 5.8 indicates the overall results of the process.

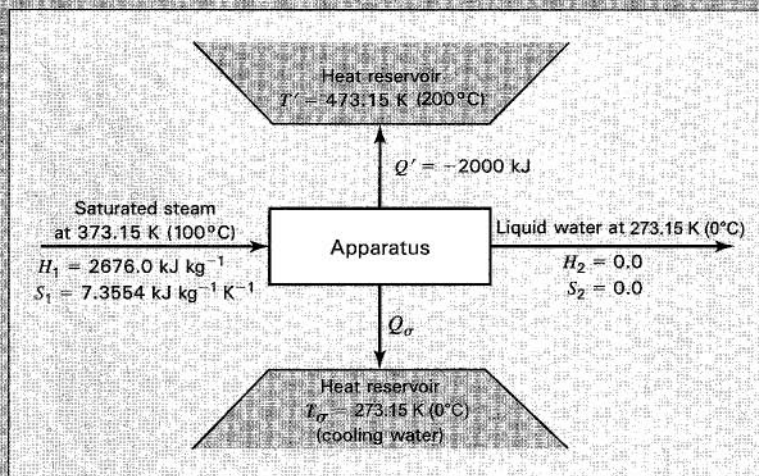


Figure 5.8 Process described in Ex. 5.6

The values of H and S for saturated steam at 373.15 K (100°C) and for liquid water at 273.15 K (0°C) are taken from the steam tables (App. F). The total heat transfer is:

$$Q = Q' + Q_{\sigma} = -2000 + Q_{\sigma}$$

Thus on the basis of 1 kg of entering steam, the first law becomes:

$$\Delta H = 0.0 - 2676.0 = -2000 + Q_{\sigma}$$

Whence,

$$Q_{\sigma} = -676.0 \text{ kJ}$$

We now examine this result in the light of the second law to determine whether ΔS_{total} is greater than or less than zero for the process. For 1 kg of steam,

$$\Delta S = 0.0 - 7.3554 = -7.3554 \text{ kJ K}^{-1}$$

For the heat reservoir at 473.15 K (200°C),

$$\Delta S' = \frac{2000}{473.15} = 4.2270 \text{ kJ K}^{-1}$$

For the heat reservoir provided by the cooling water at 273.15 K (0°C),

$$\Delta S'' = \frac{676.0}{273.15} = 2.4748 \text{ kJ K}^{-1}$$

Thus,

$$\Delta S_{\text{total}} = -7.3554 + 4.2270 + 2.4748 = -0.6536 \text{ kJ K}^{-1}$$

This result means that the process as described is impossible, because Eq. (5.19) requires $\Delta S_{\text{total}} \geq 0$.

This does not mean that all processes of this general nature are impossible, but only that the inventor has claimed too much. Indeed, the maximum amount of heat which can be transferred to the heat reservoir at 473.15 K (200°C) is readily calculated. The energy balance is:

$$Q' + Q_\sigma = \Delta H \quad (A)$$

Similarly, the entropy balance of Eq. (5.23) is

$$\Delta S = \frac{Q'}{T'} + \frac{Q_\sigma}{T_\sigma} + S_G$$

The maximum heat rejection to the hot reservoir occurs when the process is completely reversible, in which case $S_G = 0$, and

$$\frac{Q'}{T'} + \frac{Q_\sigma}{T_\sigma} = \Delta S \quad (B)$$

Combination of Eqs. (A) and (B) and solution for Q' yields:

$$Q' = \frac{T'}{T' - T_\sigma} (\Delta H - T_\sigma \Delta S)$$

With $T_\sigma = 273.15$ K and $T' = 473.15$ K, this becomes:

$$Q' = \frac{473.15}{200} (-2676.0 + 273.15 \times 7.3554) = -1577.7 \text{ kJ kg}^{-1}$$

This value of Q' is *smaller* in magnitude than the -2000 kJ kg^{-1} claimed. One also notes that the inventor's claim implies a negative rate of entropy generation.

5.8 CALCULATION OF IDEAL WORK

In any steady-state flow process requiring work, there is an absolute minimum amount which must be expended to accomplish the desired change of state of the fluid flowing through the control volume. In a process producing work, there is an absolute maximum amount which may be accomplished as the result of a given change of state of the fluid flowing through the control volume. In either case, the limiting value obtains when the change of state associated with the process is accomplished *completely reversibly*. For such a process, the entropy generation is zero, and Eq. (5.22), written for the uniform surroundings temperature T_σ , becomes:

$$\Delta(S\dot{m})_{fs} - \frac{\dot{Q}}{T_\sigma} = 0$$

or

$$Q = T_\sigma \Delta(S\dot{m})_{fs}$$

Substitute this expression for Q in the energy balance, Eq. (2.30):

$$A[(H + \frac{1}{2}u^2 + zg)\dot{m}]_{fs} = T_\sigma \Delta(S\dot{m})_{fs} + \dot{W}_s(\text{rev})$$

The shaft work, $\dot{W}_s(\text{rev})$, is here the work of a completely reversible process. If given the name *ideal work*, \dot{W}_{ideal} , the preceding equation may be rewritten:

$$\dot{W}_{\text{ideal}} = \Delta[(H + \frac{1}{2}u^2 + zg)\dot{m}]_{fs} - T_\sigma \Delta(S\dot{m})_{fs} \quad (5.24)$$

In most applications to chemical processes, the kinetic- and potential-energy terms are negligible compared with the others; in this event Eq. (5.24) reduces to:

$$W_{\text{ideal}} = \Delta(H\dot{m})_{\text{fs}} - T_{\sigma} \Delta(S\dot{m})_{\text{fs}} \quad (5.25)$$

For the special case of a single stream flowing through the control volume, Eq. (5.25) becomes:

$$W_{\text{ideal}} = \dot{m}(\Delta H - T_{\sigma} \Delta S) \quad (5.26)$$

Division by \dot{m} puts this equation on a unit-mass basis:

$$W_{\text{ideal}} = \Delta H - T_{\sigma} \Delta S \quad (5.27)$$

A completely reversible process is hypothetical, devised solely for determination of the ideal work associated with a given change of state.

The only connection between the hypothetical reversible process and an actual process is that it brings about the same change of state as the actual process.

Our objective is to compare the actual work of a process with the work of the hypothetical reversible process. No description is ever required of hypothetical processes devised for the calculation of ideal work. One need only realize that such processes may always be imagined. Nevertheless, an illustration of a hypothetical reversible process is given in Ex. 5.7.

Equations (5.24) through (5.27) give the work of a completely reversible process associated with given property changes in the flowing streams. When the same property changes occur in an actual process, the actual work \dot{W}_s (or W_s) as given by an energy balance, can be compared with the ideal work. When W_{ideal} (or \dot{W}_{ideal}) is positive, it is the *minimum work required* to bring about a given change in the properties of the flowing streams, and is smaller than \dot{W}_s . In this case a thermodynamic efficiency η_t is defined as the ratio of the ideal work to the actual work:

$$\eta_t(\text{work required}) = \frac{W_{\text{ideal}}}{\dot{W}_s} \quad (5.28)$$

When \dot{W}_{ideal} (or W_{ideal}) is negative, $|\dot{W}_{\text{ideal}}|$ is the *maximum work obtainable* from a given change in the properties of the flowing streams, and is larger than $|\dot{W}_s|$. In this case, the thermodynamic efficiency is defined as the ratio of the actual work to the ideal work:

$$\eta_t(\text{work produced}) = \frac{\dot{W}_s}{\dot{W}_{\text{ideal}}} \quad (5.29)$$

Example 5.7

What is the maximum work that can be obtained in a steady-state flow process from 1 mol of nitrogen (assumed an ideal gas) at 800 K and 50 bar? Take the temperature and pressure of the surroundings as 300 K and 1.0133 bar.

Solution 5.7

The maximum possible work is obtained from any completely reversible process that reduces the nitrogen to the temperature and pressure of the surroundings, i.e., to 300 K and 1.0133 bar. (Any gain in work done by the nitrogen because of

a final temperature or pressure below that of the surroundings would be at least equaled by the work required to produce the final condition.) What is required here is the calculation of W_{ideal} by Eq. (5.27), in which ΔS and ΔH are the molar entropy and enthalpy changes of the nitrogen as its state changes from 800 K and 50 bar to 300 K and 1.0133 bar. For an ideal gas, enthalpy is independent of pressure, and its change is given by:

$$\Delta H = \int_{T_1}^{T_2} C_p^{\text{ig}} dT$$

The value of this integral is found from Eq. (4.7), and is represented by:

$$8.314 \times \text{ICPH}(800, 300; 3.280, 0.593\text{E}-3, 0.0, 0.040\text{E}+5) = -15\,060 \text{ J mol}^{-1}$$

The parameters in the heat-capacity equation for nitrogen come from Table C.1.

Similarly, the entropy change is found from Eq. (5.14), here written:

$$\Delta S = \int_{T_1}^{T_2} C_p^{\text{ig}} \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

The value of the integral, found from Eq. (5.15), is represented by:

$$\begin{aligned} 8.314 \times \text{ICPS}(800, 300; 3.280, 0.593\text{E}-3, 0.0, 0.040\text{E}+5) \\ = -29.373 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

Whence,

$$\Delta S = -29.373 - 8.314 \ln \frac{1.0133}{50} = 3.042 \text{ J mol}^{-1} \text{ K}^{-1}$$

With these values of ΔH and ΔS , Eq. (5.27) becomes:

$$W_{\text{ideal}} = -15\,060 - (300)(3.042) = -15\,973 \text{ J mol}^{-1}$$

The significance of this simple calculation becomes evident from examination of the steps of a specific reversible process designed to bring about the given change of state. Suppose the nitrogen is continuously changed to its final state at 1.0133 bar and $T_2 = T_\sigma = 300 \text{ K}$ by the following two-step process:

- **Step 1:** Reversible, adiabatic expansion (as in a turbine) from initial state P_1, T_1, H_1 to 1.0133 bar. Let the temperature at the end of this isentropic step be T' .
- **Step 2:** Cooling (or heating, if T' is less than T_2) to the final temperature T_2 at a constant pressure of 1.0133 bar.

For step 1, a steady-state flow process, the energy balance is:

$$Q + W_s = \Delta H$$

or, since the process is adiabatic,

$$W_s = \Delta H = (H' - H_1)$$

where H' is the enthalpy at the intermediate state of T' and 1.0133 bar.

For maximum work production, step 2 must also be reversible, with heat transferred reversibly to the surroundings at T_o . These requirements are met by use of Carnot engines which receive heat from the nitrogen, produce work W_{Carnot} , and reject heat to the surroundings at T_o . Since the temperature of the heat source, the nitrogen, decreases from T' to T_2 , Eq. (5.8) for the work of a Carnot engine is written in differential form:

$$dW_{\text{Carnot}} = \frac{T - T_o}{T} (dQ)$$

Here dQ refers to the nitrogen, which is taken as the system. Integration yields:

$$W_{\text{Carnot}} = Q - T_o \int_{T'}^{T_2} \frac{dQ}{T}$$

Quantity Q , the heat exchanged with the nitrogen, is equal to the enthalpy change $H_2 - H'$. The integral is the change in entropy of the nitrogen as it is cooled by the Carnot engines. Since step 1 occurs at constant entropy, the integral also represents ΔS for both steps. Hence,

$$W_{\text{Carnot}} = (H_2 - H') - T_o \Delta S$$

The sum of W_s and W_{Carnot} gives the ideal work; thus,

$$W_{\text{ideal}} = (H' - H_1) + (H_2 - H') - T_o \Delta S = (H_2 - H_1) - T_o \Delta S$$

or

$$W_{\text{ideal}} = \Delta H - T_o \Delta S$$

which is the same as Eq. (5.27).

This derivation makes clear the difference between W_s , the ideal (reversible adiabatic) shaft work of the turbine, and W_{ideal} . The ideal work includes not only the ideal shaft work, but also all work obtainable by the operation of heat engines for the reversible transfer of heat to the surroundings at T_o .

Example 5.8

Rework Ex. 5.6, making use of the equation for ideal work.

Solution 5.8

The procedure here is to calculate the maximum possible work W_{ideal} which can be obtained from 1 kg of steam in a flow process as it undergoes a change in state from saturated steam at 373.15 K (100°C) to liquid water at 273.15 K (0°C). Now the problem reduces to the question of whether this amount of work is sufficient to operate a Carnot refrigerator rejecting 2000 kJ as heat at 473.15 K (200°C) and taking heat from the unlimited supply of cooling water at 273.15 K (0°C).

For the steam,

$$\Delta H = 0 - 2676.0 = -2676.0 \quad \Delta S = 0 - 7.3554 = -7.3554$$

With negligible kinetic- and potential-energy terms, Eq. (5.27) yields:

$$W_{\text{ideal}} = \Delta H - T_o \Delta S = -2676.0 - (273.15)(-7.3554) = -666.9 \text{ kJ kg}^{-1}$$

If this amount of work, numerically the maximum obtainable from the steam, is used to drive the Carnot refrigerator operating between the temperatures of 273.15 K (0°C) and 473.15 K (200°C), the heat rejected is found from Eq. (5.8), solved for $|Q|$:

$$|Q| = |W| \frac{T}{T_c - T} = (666.9) \left(\frac{473.15}{473.15 - 273.15} \right) = 1577.7 \text{ kJ}$$

This is the maximum possible heat release at 473.15 K (200°C); it is less than the claimed value of 2000 kJ. As in Ex. 5.6, we conclude that the process described is not possible.

5.9 LOST WORK

Work that is wasted as the result of irreversibilities in a process is called *lost work*, W_{lost} , and is defined as the difference between the actual work of a process and the ideal work for the process. Thus by definition,

$$W_{\text{lost}} \equiv W_s - W_{\text{ideal}} \quad (5.30)$$

In terms of rates,

$$\dot{W}_{\text{lost}} \equiv \dot{W}_s - \dot{W}_{\text{ideal}} \quad (5.31)$$

The actual work rate comes from Eq. (2.30):

$$\dot{W}_s = \Delta \left[\left(H + \frac{1}{2} u^2 + zg \right) \dot{m} \right]_{\text{fs}} - \dot{Q}$$

The ideal work rate is given by Eq. (5.24):

$$\dot{W}_{\text{ideal}} = A \left[\left(H + \frac{1}{2} u^2 + zg \right) \dot{m} \right]_{\text{fs}} - T_\sigma \Delta(S\dot{m})_{\text{fs}}$$

Substituting these expressions for \dot{W}_s and \dot{W}_{ideal} in Eq. (5.31) yields:

$$\dot{W}_{\text{lost}} = T_\sigma \Delta(S\dot{m})_{\text{fs}} - \dot{Q} \quad (5.32)$$

For the case of a single surroundings temperature T_σ , Eq. (5.22) becomes:

$$\dot{S}_G = \Delta(S\dot{m})_{\text{fs}} - \frac{\dot{Q}}{T_\sigma} \quad (5.33)$$

Multiplication by T_σ gives:

$$T_\sigma \dot{S}_G = T_\sigma \Delta(S\dot{m})_{\text{fs}} - \dot{Q}$$

The right sides of this equation and Eq. (5.32) are identical; therefore,

$$\dot{W}_{\text{lost}} = T_\sigma \dot{S}_G \quad (5.34)$$

Since the second law of thermodynamics requires that $\dot{S}_G \geq 0$, it follows that $W_{\text{lost}} \geq 0$. When a process is completely reversible, the equality holds, and the lost work is zero. For irreversible processes the inequality holds, and the lost work, i.e., the energy that becomes unavailable for work, is positive.

The engineering significance of this result is clear: The greater the irreversibility of a process, the greater the rate of entropy production and the greater the amount of energy that becomes unavailable for work. Thus every irreversibility carries with it a price.

For the special case of a single stream flowing through the control volume,

$$\dot{W}_{\text{lost}} = \dot{m} T_{\sigma} \Delta S - \dot{Q} \quad (5.35)$$

Division by \dot{m} makes the basis a unit amount of fluid flowing through the control volume:

$$W_{\text{lost}} = T_{\sigma} \Delta S - Q \quad (5.36)$$

Similarly, for a single stream, Eq. (5.33) becomes:

$$\dot{S}_G = \dot{m} \Delta S - \frac{\dot{Q}}{T_{\sigma}} \quad (5.37)$$

Division by \dot{m} changes the basis to a unit amount of fluid flowing through the control volume:

$$S_G = \Delta S - \frac{Q}{T_{\sigma}} \quad (5.38)$$

Equations (5.36) and (5.38) combine for a unit amount of fluid to give:

$$W_{\text{lost}} = T_{\sigma} S_G \quad (5.39)$$

Again, since $S_G \geq 0$, it follows that $W_{\text{lost}} \geq 0$.

Example 5.9

The two basic types of steady-flow heat exchanger are characterized by their flow patterns: *cocurrent* and *countercurrent*. The two types are indicated in Fig. 5.9. In cocurrent flow, heat is transferred from a hot stream, flowing from left to right, to a cold stream flowing in the same direction, as indicated by arrows. In countercurrent flow, the cold stream, again flowing from left to right, receives heat from the hot stream flowing in the opposite direction. The lines relate the temperatures of the hot and cold streams, T_H and T_C respectively, to Q_C , the accumulated rate of heat addition to the cold stream as it progresses through the exchanger from the left end to an arbitrary downstream location. Consider the two cases, for each of which the following specifications apply:

$$T_{H_1} = 400 \text{ K} \quad T_{H_2} = 350 \text{ K} \quad T_{C_1} = 300 \text{ K} \quad \dot{n}_H = 1 \text{ mol s}^{-1}$$

The minimum temperature difference between the flowing streams is 10 K. Assume that both streams are ideal gases with $C_P = (7/2)R$. Find the lost work for both cases. Take $T_{\sigma} = 300 \text{ K}$.

Solution 5.9

The following equations apply to both cases. Assume negligible kinetic- and potential-energy changes. Also $W_s = 0$, and therefore by Eq. (2.30):

$$\dot{n}_H(\Delta H)_H + \dot{n}_C(\Delta H)_C = 0$$

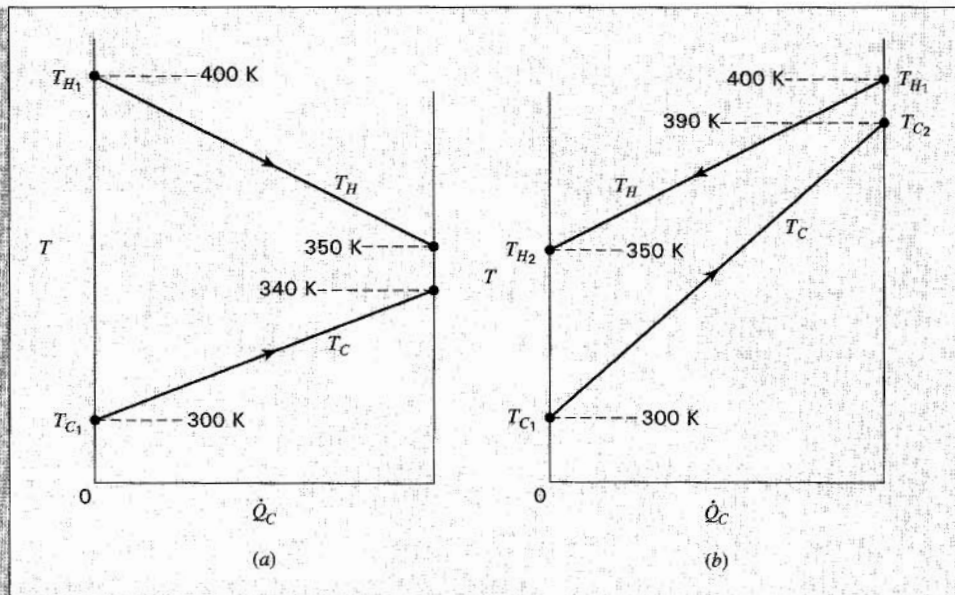


Figure 5.9 Heat exchangers. (a) Case I, cocurrent. (b) Case II, countercurrent

or in view of Eq. (3.27),

$$\dot{n}_H C_P (T_{H2} - T_{H1}) + \dot{n}_C C_P (T_{C2} - T_{C1}) = 0 \quad (A)$$

The total rate of entropy change for the flowing streams is:

$$\Delta(S\dot{n})_{fs} = \dot{n}_H (\Delta S)_H + \dot{n}_C (\Delta S)_C$$

By Eq. (5.14), with the assumption of negligible pressure change in the flowing streams, this becomes,

$$\Delta(S\dot{n})_{fs} = \dot{n}_H C_P \left(\ln \frac{T_{H2}}{T_{H1}} + \frac{\dot{n}_C}{\dot{n}_H} \ln \frac{T_{C2}}{T_{C1}} \right) \quad (B)$$

Finally, by Eq. (5.32), with negligible heat transfer to the surroundings,

$$W_{\text{lost}} = T_\sigma \Delta(S\dot{n})_{fs} \quad (C)$$

- **Case I:** Cocurrent flow. By Eq. (A),

$$\frac{\dot{n}_C}{\dot{n}_H} = \frac{400 - 350}{340 - 300} = 1.25$$

By Eq. (B),

$$\Delta(S\dot{n})_{fs} = (1)(7/2)(8.314) \left(\ln \frac{350}{400} + 1.25 \ln \frac{340}{300} \right) = 0.667 \text{ J K}^{-1} \text{ s}^{-1}$$

By Eq. (C),

$$W_{\text{lost}} = (300)(0.667) = 200.1 \text{ J s}^{-1} \text{ or W}$$

- **Case II: Countercurrent flow.** By Eq. (A),

$$\frac{\dot{n}_C}{\dot{n}_H} = \frac{400 - 350}{390 - 300} = 0.5556$$

By Eq. (B),

$$\Delta(S\dot{n})_S = (1)(7/2)(8.314) \left(\ln \frac{350}{400} + 0.5556 \ln \frac{390}{300} \right) = 0.356 \text{ J K}^{-1} \text{ s}^{-1}$$

By Eq. (C),

$$\dot{W}_{\text{lost}} = (300)(0.356) = 106.7 \text{ J s}^{-1} \text{ or W}$$

Although the total rate of heat transfer is the same for both exchangers, the temperature rise of the cold stream in countercurrent flow is more than twice that for cocurrent flow. On the other hand, the flow rate of the heated gas in the former is less than half that of the latter. From the thermodynamic point of view, the countercurrent case is much more efficient. Since $\Delta(S\dot{n})_S = \dot{S}_G$, both the rate of entropy generation and the lost work for the cocurrent case are nearly twice the values for the countercurrent case.

5.10 THE THIRD LAW OF THERMODYNAMICS

Measurements of heat capacities at very low temperatures provide data for the calculation from Eq. (5.13) of entropy changes down to 0 K. When these calculations are made for different crystalline forms of the same chemical species, the entropy at 0 K appears to be the same for all forms. When the form is noncrystalline, e.g., amorphous or glassy, calculations show that the entropy of the more random form is greater than that of the crystalline form. Such calculations, which are summarized elsewhere,² lead to the postulate that *the absolute entropy is zero for all perfect crystalline substances at absolute zero temperature*. While the essential ideas were advanced by Nernst and Planck at the beginning of the twentieth century, more recent studies at very low temperatures have increased confidence in this postulate, which is now accepted as the third law.

If the entropy is zero at $T = 0$ K, then Eq. (5.13) lends itself to the calculation of absolute entropies. With $T = 0$ as the lower limit of integration, the absolute entropy of a gas at temperature T based on calorimetric data is:

$$S = \int_0^{T_f} \frac{(C_P)_s}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_P)_l}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^T \frac{(C_P)_g}{T} dT \quad (5.40)$$

This equation³ is based on the supposition that no solid-state transitions take place and thus no heats of transition need appear. The only constant-temperature heat effects are those of fusion at T_f and vaporization at T_v . When a solid-phase transition occurs, a term $\Delta H_t/T_t$ is added.

²K. S. Pitzer, Thermodynamics, 3d ed., chap. 6, McGraw-Hill, New York, 1995.

³Evaluation of the first term on the right is not a problem for crystalline substances, because C_P/T remains finite as $T \rightarrow 0$.

5.11 ENTROPY FROM THE MICROSCOPIC VIEWPOINT

Because the molecules of an ideal gas do not interact, its internal energy resides with individual molecules. This is not true of the entropy. The microscopic interpretation of entropy is based on an entirely different concept, as suggested by the following example.

Suppose an insulated container, partitioned into two equal volumes, contains Avogadro's number N_A of ideal-gas molecules in one section and no molecules in the other. When the partition is withdrawn, the molecules quickly distribute themselves uniformly throughout the total volume. The process is an adiabatic expansion that accomplishes no work. Therefore,

$$\Delta U = C_V \Delta T = 0$$

and the temperature does not change. However, the pressure of the gas decreases by half, and the entropy change as given by Eq. (5.14) is:

$$\Delta S = -R \ln \frac{P_2}{P_1} = R \ln 2$$

Since this is the total entropy change, the process is clearly irreversible.

At the instant when the partition is removed the molecules occupy only half the space available to them. In this momentary initial state the molecules are not randomly distributed over the total volume to which they have access, but are crowded into just half the total volume. In this sense they are more ordered than they are in the final state of uniform distribution throughout the entire volume. Thus, the final state can be regarded as a more random, or more disordered, state than the initial state. Generalizing from this example, one is led to the notion that increasing disorder (or decreasing structure) on the molecular level corresponds to increasing entropy.

The means for expressing disorder in a quantitative way was developed by L. Boltzmann and J. W. Gibbs through a quantity Ω , defined as the *number of different ways* that microscopic particles can be distributed among the "states" accessible to them. It is given by the general formula:

$$\Omega = \frac{n!}{(n_1!)(n_2!)(n_3!) \cdots} \quad (5.41)$$

where n is the total number of particles, and n_1, n_2, n_3 , etc., represent the numbers of particles in "states" 1, 2, 3, etc. The term "state" denotes the condition of the microscopic particles, and the quotation marks distinguish this idea of state from the usual thermodynamic meaning as applied to a macroscopic system.

With respect to our example there are but two "states," representing location in one half or the other of the container. The total number of particles is N_A molecules, and initially they are all in a single "state." Thus

$$\Omega_1 = \frac{N_A!}{(N_A!)(0!)} = 1$$

This result confirms that initially the molecules can be distributed between the two accessible "states" in just one way. They are all in a given "state," all in just one half of the container. For an assumed final condition of uniform distribution of the molecules between the two halves of the container, $n_1 = n_2 = N_A/2$, and

$$\Omega_2 = \frac{N_A!}{[(N_A/2)!]^2}$$

This expression gives a very large number for Ω_2 , indicating that the molecules can be distributed uniformly between the two "states" in many different ways. Many other values of Ω_2 are possible, each one of which is associated with a particular nonuniform distribution of the molecules between the two halves of the container. The ratio of a particular Ω_2 to the sum of all possible values is the probability of that particular distribution.

The connection established by Boltzmann between entropy S and Ω is given by the equation:

$$S = k \ln \Omega \quad (5.42)$$

where k is Boltzmann's constant, equal to R/N_A . Integration between states 1 and 2 yields:

$$S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1}$$

Substituting values for Ω_1 and Ω_2 from our example into this expression gives:

$$S_2 - S_1 = k \ln \frac{N_A!}{[(N_A/2)!]^2} = k[\ln N_A! - 2 \ln(N_A/2)!]$$

Since N_A is very large, we take advantage of Stirling's formula for the logarithms of factorials of large numbers:

$$\ln X! = X \ln X - X$$

and as a result,

$$\begin{aligned} S_2 - S_1 &= k \left[N_A \ln N_A - N_A - 2 \left(\frac{N_A}{2} \ln \frac{N_A}{2} - \frac{N_A}{2} \right) \right] \\ &= k N_A \ln \frac{N_A}{N_A/2} = k N_A \ln 2 = R \ln 2 \end{aligned}$$

This value for the entropy change of the expansion process is the same as that given by Eq. (5.14), the classical thermodynamic formula for ideal gases.

Equations (5.41) and (5.42) are the basis for relating thermodynamic properties to statistical mechanics (Sec. 16.4).

PROBLEMS

- 5.1. Prove that it is impossible for two lines representing reversible, adiabatic processes on a PV diagram to intersect. (Hint: Assume that they do intersect, and complete the cycle with a line representing a reversible, isothermal process. Show that performance of this cycle violates the second law.)
- 5.2. A Carnot engine receives 250 kW of heat from a heat-source reservoir at 798.15 K (525°C) and rejects heat to a heat-sink reservoir at 323.15 K (50°C). What are the power developed and the heat rejected?
- 5.3. The following heat engines produce power of 95 000 kW. Determine in each case the rates at which heat is absorbed from the hot reservoir and discarded to the cold reservoir.
 - (a) A Carnot engine operates between heat reservoirs at 750 K and 300 K.
 - (b) A practical engine operates between the same heat reservoirs but with a thermal efficiency $\eta = 0.35$.

- 5.4.** A particular power plant operates with a heat-source reservoir at 623.15 K (350°C) and a heat-sink reservoir at 303.15 K (30°C). It has a thermal efficiency equal to 55% of the Carnot-engine thermal efficiency for the same temperatures.
- (a) What is the thermal efficiency of the plant?
- (b) To what temperature must the heat-source reservoir be raised to increase the thermal efficiency of the plant to 35%? Again η is 55% of the Carnot-engine value.
- 5.5.** An egg, initially at rest, is dropped onto a concrete surface; it breaks. Prove that the process is irreversible. In modeling this process treat the egg as the system, and assume the passage of sufficient time for the egg to return to its initial temperature.
- 5.6.** Which is the more effective way to increase the thermal efficiency of a Carnot engine: to increase T_H with T_C constant, or to decrease T_C with T_H constant? For a real engine, which would be the more *practical* way?
- 5.7.** Large quantities of liquefied natural gas (*LNG*) are shipped by ocean tanker. At the unloading port provision is made for vaporization of the *LNG* so that it may be delivered to pipelines as gas. The *LNG* arrives in the tanker at atmospheric pressure and 113.7 K , and represents a possible heat sink for use as the cold reservoir of a heat engine. For unloading of *LNG* as a vapor at the rate of $9000\text{ m}^3\text{ s}^{-1}$, as measured at 298.15 K (25°C) and 1.0133 bar , and assuming the availability of an adequate heat source at 303.15 K (30°C), what is the maximum possible power obtainable and what is the rate of heat transfer from the heat source? Assume that *LNG* at 298.15 K (25°C) and 1.0133 bar is an ideal gas with the molar mass of 17. Also assume that the *LNG* vaporizes only, absorbing only its latent heat of 512 kJ kg^{-1} at 113.7 K .
- 5.8.** With respect to 1 kg of liquid water:
- (a) Initially at 273.15 K (0°C), it is heated to 373.15 K (100°C) by contact with a heat reservoir at 373.15 K (100°C). What is the entropy change of the water? Of the heat reservoir? What is ΔS_{total} ?
- (b) Initially at 273.15 K (0°C), it is first heated to 323.15 K (50°C) by contact with a heat reservoir at 323.15 K (50°C) and then to 373.15 K (100°C) by contact with a reservoir at 373.15 K (100°C). What is ΔS_{total} ?
- (c) Explain how the water might be heated from 273.15 K (0°C) to 373.15 K (100°C) so that $\Delta S_{\text{total}} = 0$.
- 5.9.** A rigid vessel of 0.06 m^3 volume contains an ideal gas, $C_V = (5/2)R$, at 500 K and 1 bar.
- (a) If heat in the amount of 15 kJ is transferred to the gas, determine its entropy change.
- (b) If the vessel is fitted with a stirrer that is rotated by a shaft so that work in the amount of 15 kJ is done on the gas, what is the entropy change of the gas if the process is adiabatic? What is ΔS_{total} ? What is the irreversible feature of the process?
- 5.10.** An ideal gas, $C_P = (7/2)R$, is heated in a steady-flow heat exchanger from 343.15 K to 463.15 K (70°C to 190°C) by another stream of the same ideal gas which enters at 593.15 K (320°C). The flow rates of the two streams are the same, and heat losses from the exchanger are negligible.

- (a) Calculate the molar entropy changes of the two gas streams for both parallel and countercurrent flow in the exchanger.
 (b) What is ΔS_{total} in each case?
 (c) Repeat parts (a) and (b) for countercurrent flow if the heating stream enters at 473.15 K (200°C).

5.11. For an ideal gas with constant heat capacities, show that:

- (a) For a temperature change from T_1 to T_2 , ΔS of the gas is greater when the change occurs at constant pressure than when it occurs at constant volume.
 (b) For a pressure change from P_1 to P_2 , the sign of ΔS for an isothermal change is opposite that for a constant-volume change.

5.12. For an ideal gas prove that:

$$\frac{\Delta S}{R} = \int_{T_0}^T \frac{C_V^{ig}}{R} \frac{dT}{T} + \ln \frac{V}{V_0}$$

5.13. A Carnot engine operates between two finite heat reservoirs of total heat capacity C_H^t and C_C^t .

- (a) Develop an expression relating T_C to T_H at any time.
 (b) Determine an expression for the work obtained as a function of C_H^t , C_C^t , T_H , and the initial temperatures T_{H_0} and T_{C_0} .
 (c) What is the maximum work obtainable? This corresponds to infinite time, when the reservoirs attain the same temperature.

In approaching this problem, use the differential form of Carnot's equation,

$$\frac{dQ_H}{dQ_C} = - \frac{T_H}{T_C}$$

and a differential energy balance for the engine,

$$dW - dQ_C - dQ_H = 0$$

Here, Q_C and Q_H refer to the reservoirs.

5.14. A Carnot engine operates between an infinite hot reservoir and a *finite* cold reservoir of total heat capacity C_C^t .

- (a) Determine an expression for the work obtained as a function of C_C^t , T_H (= constant), T_C , and the initial cold-reservoir temperature T_{C_0} .
 (b) What is the *maximum* work obtainable? This corresponds to infinite time, when T_C becomes equal to T_H .

The approach to this problem is the same as for Pb. 5.13.

5.15. A heat engine operating in outer space may be assumed equivalent to a Carnot engine operating between reservoirs at temperatures T_H and T_C . The only way heat can be discarded from the engine is by radiation, the rate of which is given (approximately) by:

$$|\dot{Q}_C| = kAT_C^4$$

where k is a constant and A is the area of the radiator. Prove that, for fixed power output $|\dot{W}|$ and for fixed temperature T_H , the radiator area A is a minimum when the temperature ratio T_C/T_H is 0.75.

- 5.16.** Imagine that a stream of fluid in steady-state flow serves as a heat source for an infinite set of Carnot engines, each of which absorbs a differential amount of heat from the fluid, causing its temperature to decrease by a differential amount, and each of which rejects a differential amount of heat to a heat reservoir at temperature T . As a result of the operation of the Carnot engines, the temperature of the fluid decreases from T_1 to T_2 . Equation (5.8) applies here in differential form, wherein η is defined as:

$$\eta \equiv dW/dQ$$

where Q is heat transfer with respect to the flowing fluid. Show that the total work of the Carnot engines is given by:

$$W = Q - T_\sigma \Delta S$$

where ΔS and Q both refer to the fluid. In a particular case the fluid is an ideal gas, $C_p = (7/2)R$, for which $T_1 = 600$ K and $T_2 = 400$ K. If $T_\sigma = 300$ K, what is the value of W in $J \text{ mol}^{-1}$? How much heat is discarded to the heat reservoir at T ? What is the entropy change of the heat reservoir? What is ΔS_{total} ?

- 5.17.** A Carnot engine operates between temperature levels of 600 K and 300 K. It drives a Carnot refrigerator, which provides cooling at 250 K and discards heat at 300 K. Determine a numerical value for the ratio of heat extracted by the refrigerator ("cooling load") to the heat delivered to the engine ("heating load").
- 5.18.** An ideal gas with constant heat capacities undergoes a change of state from conditions T_1, P_1 to conditions T_2, P_2 . Determine ΔH ($J \text{ mol}^{-1}$) and ΔS ($J \text{ mol}^{-1} \text{ K}^{-1}$) for one of the following cases.
- (a) $T_1 = 300$ K, $P_1 = 1.2$ bar, $T_2 = 450$ K, $P_2 = 6$ bar, $C_p/R = 7/2$.
 (b) $T_1 = 300$ K, $P_1 = 1.2$ bar, $T_2 = 500$ K, $P_2 = 6$ bar, $C_p/R = 7/2$.
 (c) $T_1 = 450$ K, $P_1 = 10$ bar, $T_2 = 300$ K, $P_2 = 2$ bar, $C_p/R = 5/2$.
 (d) $T_1 = 400$ K, $P_1 = 6$ bar, $T_2 = 300$ K, $P_2 = 1.2$ bar, $C_p/R = 9/2$.
 (e) $T_1 = 500$ K, $P_1 = 6$ bar, $T_2 = 300$ K, $P_2 = 1.2$ bar, $C_p/R = 4$.

- 5.19.** An ideal gas, $C_p = (7/2)R$ and $C_v = (5/2)R$, undergoes a cycle consisting of the following mechanically reversible steps:

- An adiabatic compression from P_1, V_1, T_1 to P_2, V_2, T_2 .
- An isobaric expansion from P_2, V_2, T_2 to $P_3 = P_2, V_3, T_3$.
- An adiabatic expansion from P_3, V_3, T_3 to P_4, V_4, T_4 .
- A constant-volume process from P_4, V_4, T_4 to $P_1, V_1 = V_4, T_1$.

Sketch this cycle on a PV diagram and determine its thermal efficiency if $T_1 = 473.15$ K (200°C), $T_2 = 773.15$ K (500°C), $T_3 = 1973.15$ K (1700°C), and $T_4 = 973.15$ K (700°C).

- 5.20.** The infinite heat reservoir is an abstraction, often approximated in engineering applications by large bodies of air or water. Apply the closed-system form of the energy balance [Eq. (2.3)] to such a reservoir, treating it as a constant-volume system. How is it that heat transfer to or from the reservoir can be nonzero, yet the temperature of the reservoir remains constant?

5.21. One mole of an ideal gas, $C_P = (7/2)R$ and $C_V = (5/2)R$, is compressed adiabatically in a piston/cylinder device from 2 bar and 298.15 K (25°C) to 7 bar. The process is irreversible and requires 35% more work than a reversible, adiabatic compression from the same initial state to the same final pressure. What is the entropy change of the gas?

5.22. A mass m of liquid water at temperature T_1 is mixed adiabatically and isobarically with an equal mass of liquid water at temperature T_2 . Assuming constant C_P , show that

$$\Delta S' = \Delta S_{\text{total}} = S_G = 2mC_P \ln \frac{(T_1 + T_2)/2}{(T_1 T_2)^{1/2}}$$

and prove that this is positive. What would be the result if the masses of the water were *different*, say, m_1 and m_2 ?

5.23. Reversible adiabatic processes are isentropic. Are isentropic processes necessarily reversible and adiabatic? If so, explain why; if not, give an example illustrating the point.

5.24. Prove that the mean heat capacities $\langle C_P \rangle_H$ and $\langle C_P \rangle_S$ are inherently positive, whether $T > T_0$ or $T < T_0$. Explain why they are well defined for $T = T_0$.

5.25. A reversible cycle executed by 1 mol of an ideal gas for which $C_P = (5/2)R$ and $C_V = (3/2)R$ consists of the following:

- Starting at $T_1 = 700$ K and $P_1 = 1.5$ bar, the gas is cooled at constant pressure to $T_2 = 350$ K.
- From 350 K and 1.5 bar, the gas is compressed isothermally to pressure P_2 .
- The gas returns to its initial state along a path for which $PT = \text{constant}$.

What is the thermal efficiency of the cycle?

5.26. One mole of an ideal gas is compressed isothermally but irreversibly at 403.15 K (130°C) from 2.5 bar to 6.5 bar in a piston/cylinder device. The work required is 30% greater than the work of reversible, isothermal compression. The heat transferred from the gas during compression flows to a heat reservoir at 298.15 K (25°C). Calculate the entropy changes of the gas, the heat reservoir, and ΔS_{total} .

5.27. For a steady-flow process at approximately atmospheric pressure, what is the entropy change of the gas:

- (a) When 10 mol of SO_2 is heated from 473.15 to 1373.15 K (200 to 1100°C)?
- (b) When 12 mol of propane is heated from 523.15 to 1473.15 K (250 to 1200°C)?

5.28. What is the entropy change of the gas, heated in a steady-flow process at approximately atmospheric pressure,

- (a) When 800 kJ is added to 10 mol of ethylene initially at 473.15 K (200°C)?
- (b) When 2500 kJ is added to 15 mol of 1-butene initially at 533.15 K (260°C)?
- (c) When 1.055 GJ is added to 18.14 kmol of ethylene initially at 533.15 K (260°C)?

5.29. A device with no moving parts provides a steady stream of chilled air at 248.15 K (−25°C) and 1 bar. The feed to the device is compressed air at 298.15 K (25°C) and 5 bar. In addition to the stream of chilled air, a second stream of warm air

flows from the device at 348.15 K (75°C) and 1 bar. Assuming adiabatic operation, what is the ratio of chilled air to warm air that the device produces? Assume that air is an ideal gas for which $C_P = (7/2)R$.

- 5.30.** An inventor has devised a complicated nonflow process in which 1 mol of air is the working fluid. The net effects of the process are claimed to be:
- A change in state of the air from 523.15 K (250°C) and 3 bar to 353.15 K (80°C) and 1 bar.
 - The production of 1800 J of work.
 - The transfer of an undisclosed amount of heat to a heat reservoir at 303.15 K (30°C).

Determine whether the claimed performance of the process is consistent with the second law. Assume that air is an ideal gas for which $C_P = (7/2)R$.

- 5.31.** Consider the heating of a house by a furnace, which serves as a heat-source reservoir at a high temperature T_F . The house acts as a heat-sink reservoir at temperature T , and heat $|Q|$ must be added to the house during a particular time interval to maintain this temperature. Heat $|Q|$ can of course be transferred directly from the furnace to the house, as is the usual practice. However, a third heat reservoir is readily available, namely, the surroundings at temperature T_σ , which can serve as another heat source, thus reducing the amount of heat required from the furnace. Given that $T_F = 810$ K, $T = 295$ K, $T_\sigma = 265$ K, and $|Q| = 1000$ kJ, determine the minimum amount of heat $|Q_F|$ which must be extracted from the heat-source reservoir (furnace) at T_F . No other sources of energy are available.
- 5.32.** Consider the air conditioning of a house through use of solar energy. At a particular location experiment has shown that solar radiation allows a large tank of pressurized water to be maintained at 448.15 K (175°C). During a particular time interval, heat in the amount of 1500 kJ must be extracted from the house to maintain its temperature at 297.15 K (24°C) when the surroundings temperature is 306.15 K (33°C). Treating the tank of water, the house, and the surroundings as heat reservoirs, determine the minimum amount of heat that must be extracted from the tank of water by any device built to accomplish the required cooling of the house. No other sources of energy are available.
- 5.33.** A refrigeration system cools a brine from 298.15 K to 258.15 K (25°C to -15°C) at the rate 20 kg s^{-1} . Heat is discarded to the atmosphere at a temperature of 303.15 K (30°C). What is the power requirement if the thermodynamic efficiency of the system is 0.27? The specific heat of the brine is $3.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$.
- 5.34.** An electric motor under steady load draws 9.7 amperes at 110 volts; it delivers 0.93 kW of mechanical energy. The temperature of the surroundings is 300 K. What is the total rate of entropy generation in W K^{-1} ?
- 5.35.** A 25-ohm resistor at steady state draws a current of 10 amperes. Its temperature is 310 K; the temperature of the surroundings is 300 K. What is the total rate of entropy generation \dot{S}_G ? What is its origin?
- 5.36.** Show how the general rate form of the entropy balance, Eq. (5.21), reduces to Eq. (5.19) for the case of a closed system.

5.37. A list of common unit operations follows:

- (a) Single-pipe heat exchanger; (b) Double-pipe heat exchanger; (c) Pump;
 (d) Gas compressor; (e) Gas turbine (expander); (f) Throttle valve; (g) Nozzle.

Develop a simplified form of the general steady-state entropy balance appropriate to each operation. State carefully, and justify, any assumptions you make.

5.38. Ten kmol per hour of air is throttled from upstream conditions of 298.15 K (25°C) and 10 bar to a downstream pressure of 1.2 bar. Assume air to be an ideal gas with $C_P = (7/2)R$.

- (a) What is the downstream temperature?
 (b) What is the entropy change of the air in $\text{J mol}^{-1} \text{K}^{-1}$?
 (c) What is the rate of entropy generation in W K^{-1} ?
 (d) If the surroundings are at 293.15 K (20°C), what is the lost work?

5.39. A steady-flow adiabatic turbine (expander) accepts gas at conditions T_1 , P_1 , and discharges at conditions T_2 , P_2 . Assuming ideal gases, determine (per mole of gas) W , W_{ideal} , W_{lost} , and S_G for one of the following cases. Take $T_\sigma = 300 \text{ K}$.

- (a) $T_1 = 500 \text{ K}$, $P_1 = 6 \text{ bar}$, $T_2 = 371 \text{ K}$, $P_2 = 1.2 \text{ bar}$, $C_P/R = 7/2$.
 (b) $T_1 = 450 \text{ K}$, $P_1 = 5 \text{ bar}$, $T_2 = 376 \text{ K}$, $P_2 = 2 \text{ bar}$, $C_P/R = 4$.
 (c) $T_1 = 525 \text{ K}$, $P_1 = 10 \text{ bar}$, $T_2 = 458 \text{ K}$, $P_2 = 3 \text{ bar}$, $C_P/R = 11/2$.
 (d) $T_1 = 475 \text{ K}$, $P_1 = 7 \text{ bar}$, $T_2 = 372 \text{ K}$, $P_2 = 1.5 \text{ bar}$, $C_P/R = 9/2$.
 (e) $T_1 = 550 \text{ K}$, $P_1 = 4 \text{ bar}$, $T_2 = 403 \text{ K}$, $P_2 = 1.2 \text{ bar}$, $C_P/R = 5/2$.

5.40. Consider the direct heat transfer from a heat reservoir at T_1 to another heat reservoir at temperature T_2 , where $T_1 > T_2 > T_\sigma$. It is not obvious why the lost work of this process should depend on T_σ , the temperature of the surroundings, because the surroundings are not involved in the actual heat-transfer process. Through appropriate use of the Carnot-engine formula, show for the transfer of an amount of heat equal to $|Q|$ that

$$W_{\text{lost}} = T_\sigma |Q| \frac{T_1 - T_2}{T_1 T_2} = T_\sigma S_G$$

5.41. An ideal gas at 2500 kPa is throttled adiabatically to 150 kPa at the rate of 20 mol s^{-1} . Determine \dot{S}_G and \dot{W}_{lost} if $T_\sigma = 300 \text{ K}$.

5.42. An inventor claims to have devised a cyclic engine which exchanges heat with reservoirs at 298.15 K to 523.15 K (25°C and 250°C), and which produces 0.45 kJ of work for each kJ of heat extracted from the hot reservoir. Is the claim believable?

5.43. Heat in the amount of 150 kJ is transferred directly from a hot reservoir at $T_H = 550 \text{ K}$ to two cooler reservoirs at $T_1 = 350 \text{ K}$ and $T_2 = 250 \text{ K}$. The surroundings temperature is $T_\sigma = 300 \text{ K}$. If the heat transferred to the reservoir at T_1 is half that transferred to the reservoir at T_2 , calculate:

- (a) The entropy generation in kJ K^{-1} .
 (b) The lost work.

How could the process be made reversible?

5.44. A nuclear power plant generates 750 MW; the reactor temperature is 588.15 K (315°C) and a river with water temperature of 293.15 K (20°C) is available.

- (a) What is the maximum possible thermal efficiency of the plant, and what is the minimum rate at which heat must be discarded to the river?
- (b) If the actual thermal efficiency of the plant is 60% of the maximum, at what rate must heat be discarded to the river, and what is the temperature rise of the river if it has a flowrate of $165 \text{ m}^3 \text{ s}^{-1}$?
- 5.45.** A single gas stream enters a process at conditions T_1 , P_1 , and leaves at pressure P_2 . The process is adiabatic. Prove that the outlet temperature T_2 for the actual (irreversible) adiabatic process is greater than that for a *reversible* adiabatic process. Assume the gas is ideal with constant heat capacities.