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Second Law of Thermodynamics and Entropy

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Second Law of Thermodynamics and Entropy

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Thermodynamics is founded on a number of axioms, laws that have not been proven in a general sense but seem to agree with all of the experimental observations of natural phenomena conducted so far. Most commonly, these axioms are formulated under the names of the first, second, third, and zeroth laws of thermodynamics, but other axiomatic definitions have been formulated and shown to be equally successful [see Callen, 1985].

The first law of thermodynamics is a statement of energy conservation, mathematically providing an energy-accounting equation useful in the analysis of **thermodynamic systems** and generally enlightening us about energy conservation and the axiom that, as far as energy is concerned, one cannot get something for nothing. It does not, however, provide guidance about the directions and limitations of the work, heat, and other energy conversion interactions in the process under consideration. For example, the assignment of an amount of heat (positive or negative) in a first law equation is not conditioned on whether that amount of heat is delivered from a low-temperature source to a high-temperature one or vice versa; heat, work, and other forms of energy are treated as having the same thermodynamic quality, and there is no restriction on how much of the heat input could be converted into work as long as overall energy conservation is maintained. The second law provides these types of guidance and thus more strongly distinguishes thermodynamics from its subset branches of physics, such as mechanics.

Several competing statements and practical corollaries of the second law have been developed over the years. They are all consistent with each other. Those that have more rigor and generality are also typically somewhat more obscure to the practitioner, whereas those that are stated in simpler and more practical terms, though still correct, do not encompass all possible processes.

The best known statement of the second law is the Kelvin–Planck one: "It is impossible to construct an engine that, operating in a **cycle**, will produce no effect other than the extraction of heat from a single **reservoir** and the performance of an equivalent amount of work." If such an engine, depicted in Figure 46.1(a), would be feasible, the produced work could then be returned to the reservoir. As a consequence of these operations, the reservoir, originally in equilibrium, is now in a new state, whereas the engine
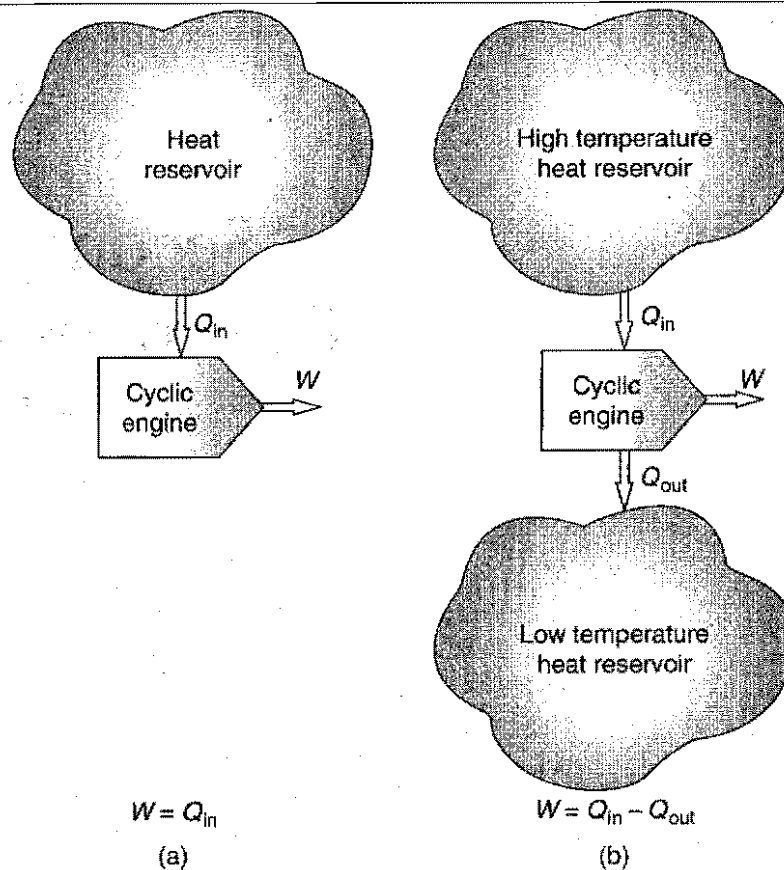
FIGURE 46.1 Comparison of power cycles (a) disallowed and (b) allowed by the second law: (a) a perpetual motion machine of the second kind (PMM2); (b) allowed power cycle.

(being cyclic) and the environment have not changed. Since a system in equilibrium (here the reservoir) can only be disequilibrated as a result of a change in its environment, the only way to satisfy the second law is by denying the possibility of a so-called *perpetual motion machine of the second kind* (PMM2) that, after having been started, produces work continuously without any net investment of energy. Rephrased, the Kelvin–Planck form of the second law thus states that a PMM2 is impossible, and, most notably, that a given quantity of heat cannot fully be converted to work: the heat-to-work conversion efficiency is always lower than 100%. Strikingly, no thermodynamic efficiency restriction exists in the opposite direction of the process: work energy can be fully converted into heat.

A work-producing cyclical engine that does not defy that second law is depicted in Figure 46.1(b). Besides making work, it has an effect of rejecting a portion of the heat gained from the heat source reservoir to a heat sink reservoir. This heat rejection causes an equivalent reduction of the amount of work produced, as dictated by the first law.

Another useful statement of the second law was made by Clausius: "It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a region of lower temperature to a region of higher temperature." If such a device, depicted in Figure 46.2(a), would be feasible, it would allow the transfer of heat from colder to warmer regions without any investment of work. Combined with the cycle of Figure 46.1(b), it would then:

1. Allow the operation of a perpetual motion machine
2. Allow the operation of refrigerators that require no work investment, and
3. Defy the empirical laws of heat transfer, which insist that heat is transferred only down the temperature gradient — from hot to cold regions — and not in the opposite direction

A cooling cycle that does not defy the second law is depicted in Figure 46.2(b). In addition to cooling (taking heat from) the lower-temperature reservoir and delivering that amount of heat to the higher-
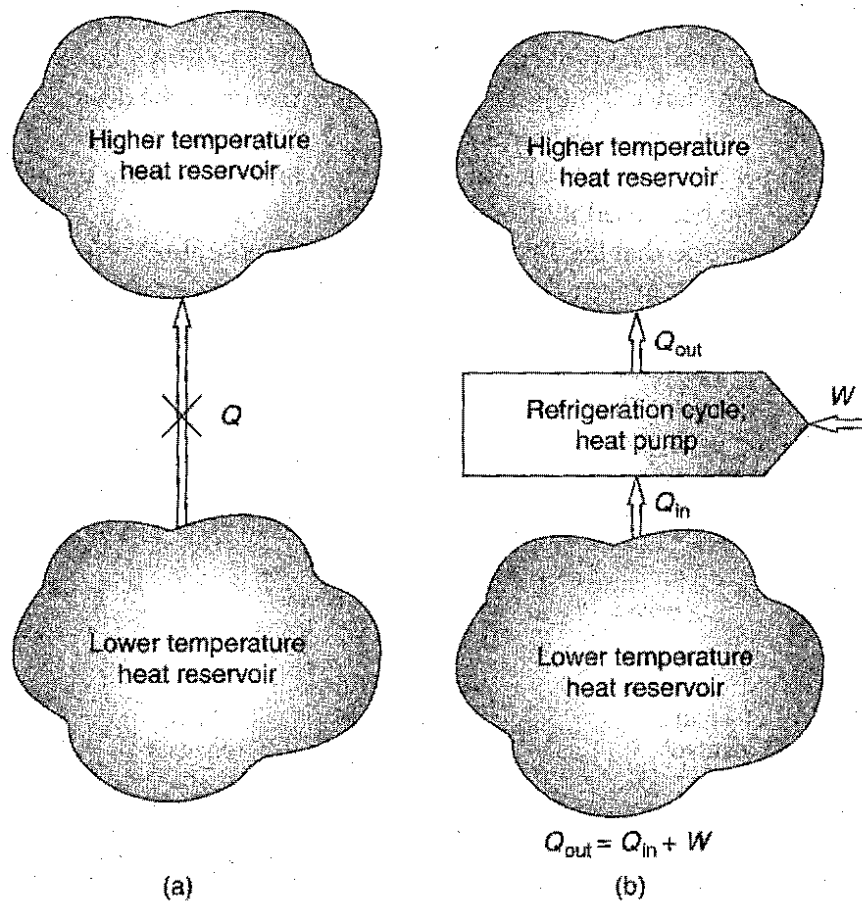
FIGURE 46.2 Comparison of conditions under which heat flow from low temperature to a higher temperature is (a) disallowed and (b) allowed by the second law: (a) heat flow from low to high temperature disallowed by the second law if the system environment does not change; (b) heat flow from low to high temperature allowed by the second law if work is supplied from the environment.

temperature reservoir, it has an effect of requiring some work from the outside, with an equivalent increase in the amount of heat delivered to the high-temperature reservoir, as dictated by the first law.

Two of the most rigorous statements of the second law are given as follows. Carathéodory proposed that "In the neighborhood of a **state** of a system there are states the system cannot reach through **adiabatic** processes" [Hatsopoulos and Keenan, 1965]. Furthermore, "A system having specified allowed states and an upper bound in volume can reach from any given state a **stable state** and leave no net effect on the **environment**" [Hatsopoulos and Keenan, 1965]. As explained already, it can be proven that these statements of the second law are fully consistent with the previous ones, in essence pronouncing axiomatically here that *stable equilibrium states exist*. A rudimentary exposition of the link between this statement and the impossibility of a PMM2 has been given in the preceding, and further clarification is available in the cited references.

46.1 Reversibility

After the disturbing second law statement that heat cannot fully be converted into work, the next logical question concerns the maximal efficiency of such energy conversion. It is obvious from the first law, and even just from operational considerations, that the most efficient heat-to-work conversion process is one that incurs minimal diversions of energy into paths that do not eventually produce work. In a generalized heat-to-work conversion process such as that in Figure 46.1(b), its components are two heat reservoirs at different temperatures, some type of device that produces work when interacting with these two heat reservoirs, and a sink for the produced work. It involves two heat transfer processes (one from the hot reservoir to the device, and one from the device to the cold reservoir), some heat-to-work conversion

process inside the device, and a work transfer process from the device to the work sink. Losses in the amount of energy available for work production occur in practice in each of these processes. The most obvious from operational experience is the loss due to possible friction in the device, in the transfer from it to the work-sink, and in any fluid flow associated with the process. Friction converts work into heat and thus diminishes the net amount of work produced. From another vantage point, the force used to overcome friction could have been used to produce work.

Many other phenomena, somewhat less operationally apparent, may also cause such losses. For example, it is easy to show that any heat transfer across a finite temperature difference causes a loss in the ability to produce work: if, as illustrated in Figure 46.3(a), the device producing work W is at the temperature T_d, where $T_c < T_d < T_h$, one could have conceivably incorporated an additional heat-to-work conversion device between each of the two heat reservoirs and the original device, as shown in Figure 46.3(b), and produced more work ($W + W_h + W_c$) than the system shown in Figure 46.3(b). These losses approach zero when the temperature differences between the heat reservoirs and the respective regions of the device with which they have a heat interaction also approach zero.
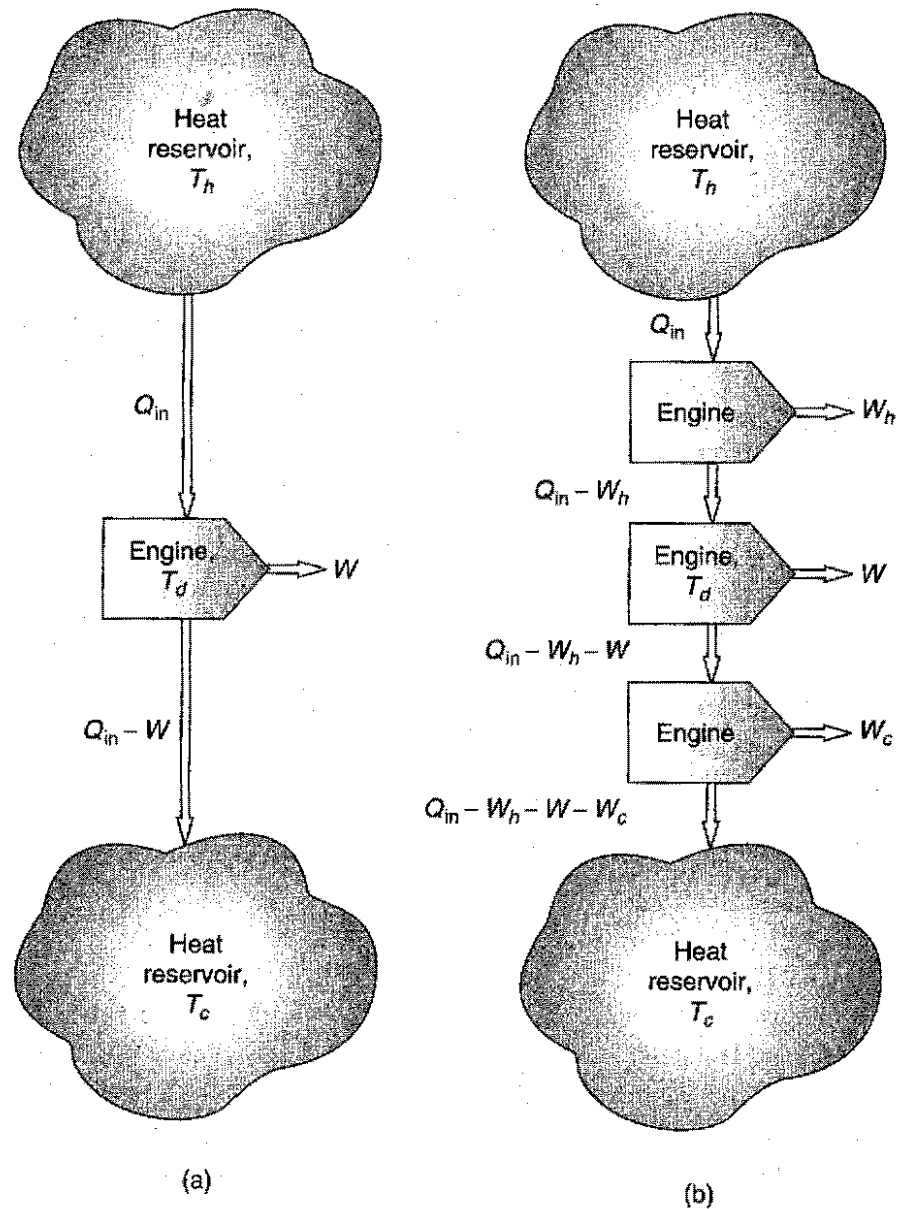

(a)   (b)

FIGURE 46.3 Power production with reservoir-engine heat transfer across finite temperature differences, $T_c < T_d < T_h$: (a) work produced is only W; (b) work produced is $W + W_h + W_c$.
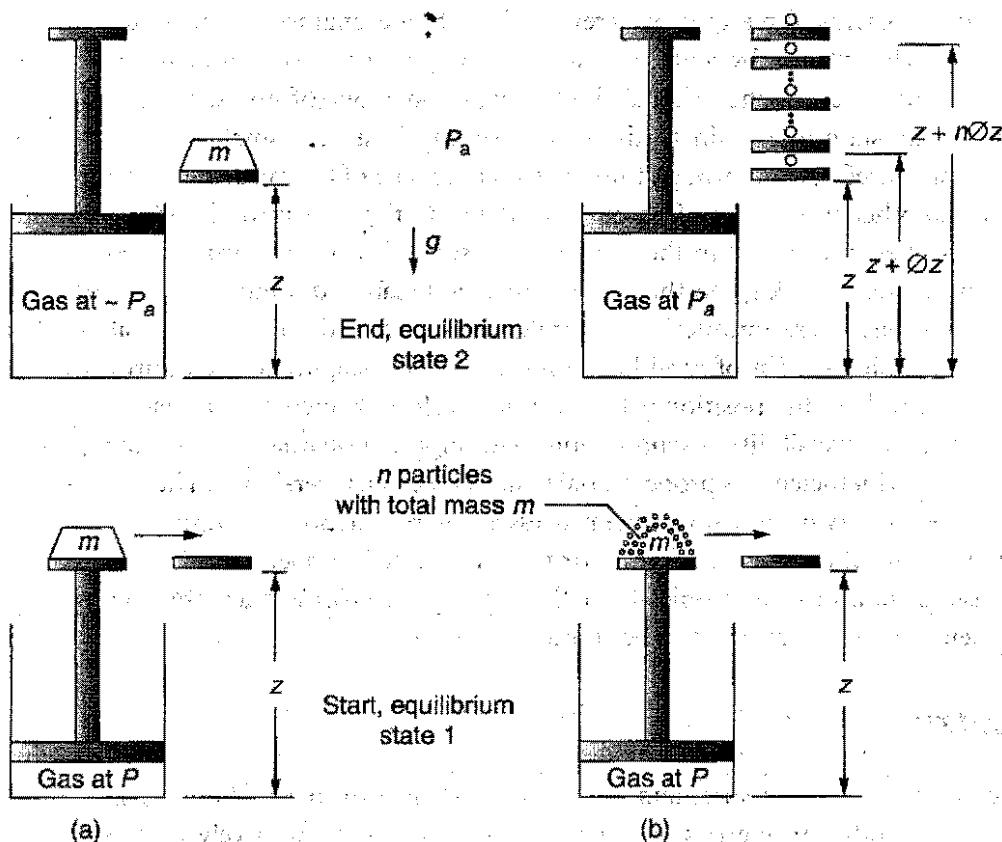
FIGURE 46.4 Illustration of the approach to reversibility: (a) abrupt expansion with no weight raise, no useful work production (highly irreversible process); (b) gradual expansion with weight raise, some useful work production (more reversible process).

Having established that temperature difference (or more strictly, temperature gradient) is a thermodynamic driving potential for work production, one can easily recognize that there are other thermodynamic potentials for work production, such as pressure gradients (piston engines and turbines, for example), concentration gradients (batteries and fuel cells), and electric potential gradients (electric motors). Analogous to the arguments presented for losses due to finite temperature differences, it is easy to recognize that similar losses occur due to phenomena such as unrestrained expansion, the mixing of two different substances, the diffusion of a single substance in a mixture across a finite concentration difference, and the passage of current across an electric potential gradient, all when unaccompanied by commensurate production of work.

It is interesting to note that the work-production losses due to all of these processes approach zero if the respective thermodynamic driving potentials approach zero. Furthermore, processes that proceed toward the new equilibrium state due to the influence of a succession of such infinitesimally small driving potentials can in the limit also be reversed in direction without any residual change in the system and its environment. A good example is a frictionless system in which some amount of gas confined in a cylinder is held at a pressure larger than the ambient pressure by means of a piston loaded down with a weight, as shown in Figure 46.4(a). To simplify the example, let us also assume that the system is originally at ambient temperature and that it is perfectly thermally insulated from the environment. Let us judge the ability of the system to do work by the height that it can lift some weight. If the weight is effortlessly slid to the side (in a direction perpendicular to gravity), the piston would pop up to the new force equilibrium state, under which the gas has expanded to a higher volume and lower pressure and temperature, but since the weight has remained at its original level the system has performed no useful work. The reversal of the process to bring the system *and the environment* to their original condition cannot be done, because work would have to be supplied for that purpose from the environment, thus changing its original state. This is an example of a process at its worst — producing no useful work and characterized

by a large (finite) driving force and by irreversibility. Some engineering ingenuity can improve the situation vastly, in the extreme by replacing the single weight with a very large number of small weights having the same total mass as the original single weight, say a pile of fine sand grains [Figure 46.4(b)]. Now we effortlessly slide one grain to the side, resulting in a very small rise of the piston and the production of some useful work through the consequent raising of the sand pile *sans* one grain. Removing one grain after another in the same fashion until the last grain is removed and the piston rests at the same equilibrium height as it did in the previously described worthless process will, as seems obvious, produce the most useful work given the original thermodynamic driving force. Furthermore, since the movements of the piston are infinitesimally small, one could, without any residual effect on the environment, slide each lifted grain of sand back onto the piston slightly to recompress the gas and move the piston down a little to the position it has occupied before its incremental rise.

Generalizing, then, reversibility is synonymous with highest potential for producing useful work, and the degree of process inefficiency is proportional to its degree of irreversibility. The example also illustrates the practical impossibility of fully reversible processes: the production of a finite amount of work at this maximal efficiency would either take forever or take an infinite number of such pistons, each lifting one grain at the same time (and frictionlessly at that). Practical processes are thus always a compromise between efficiency, rate, and amount of equipment needed.

46.2 Entropy

Like volume, temperature, pressure, and energy, entropy is a property characterizing thermodynamic systems. Unlike the other properties, it is not operationally and intuitively understood by novices, a situation not made simpler by the various approaches to its fundamental definition and by its increasing cavalier metaphysical application to fields as disparate as information theory, social science, economics, religion, and philosophy. Let us begin with the fundamental, prosaic definition of entropy, S, as

$$dS = \left(\frac{\delta Q}{T}\right)_{rev} \tag{46.1}$$

showing that the differential change in entropy, dS, in a process is equal to the ratio of the differential amount of heat interaction, δQ, that takes place if the process is reversible and the absolute temperature, T, during that process. For a finite-extent process between thermodynamic states 1 and 2, Equation (46.1) can be integrated to give

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} \tag{46.2}$$

It is noteworthy here that, since entropy is a property and thus uniquely defined at states 1 and 2, the entropy change between these two states is always the same, whether the process is reversible or irreversible.

Entropy values of various materials are available in the literature: most books on thermodynamics and chemical and mechanical engineering handbooks include values of the entropy as a function of temperature and pressure; an extensive source for gas properties particularly related to high-temperature processes are the JANAF tables [Stull and Prophet, 1971]. The entropy values are given based on a common (but somewhat arbitrary) reference state, and its units are typically kJ/kg K, Btu/lb R, or kJ/kmol K if a molar basis is used. Although not used much in engineering practice, the fundamental reference state of entropy is 0 K, where according to the third law of thermodynamics the entropy tends to 0.

If the process between states 1 and 2 is irreversible, then

$$\left(\frac{\delta Q}{T}\right)_{irrev} \neq \left(\frac{\delta Q}{T}\right)_{rev} \tag{46.3}$$

and it can be shown by using the second law that

$$S_2 - S_1 \geq \int_1^2 \left(\frac{\delta Q}{T} \right) \tag{46.4}$$

where the equality sign applies to reversible processes and the inequality to irreversible ones. Consequently, it can also be shown for isolated systems (i.e., those having no interactions with their environment) that

$$dS_{\text{isolated system}} \geq 0 \tag{46.5}$$

where again the equality sign applies to reversible processes and the inequality to irreversible ones. Since a thermodynamic system and its environment together form an isolated system by definition, Equation (46.5) also states that the sum of the entropy changes of the system and the environment is ≥ 0.

In another axiomatic approach to thermodynamics [Callen, 1985], the existence of the entropy property is introduced as an axiom and not as a derived property defined by Equation (46.1). It is basically postulated that, out of all the new equilibrium states that the system may attain at the end of a process, the one that has the maximal entropy will be realized. Equation (46.1) and other more familiar consequences of entropy are then derived as corollaries of this maximum postulate.

Equation (46.5) and the other attributes of entropy lead to several eminent mathematical, physical, and other consequences. Mathematically, the inequality Equation (46.5) indicates that many solutions may exist, which are bounded by the equality limit. In other words, out of all the new states 2 that an isolated system starting from state 1 can reach, only those at which the system entropy is larger are allowed; a unique (but practically unreachable) state 2 can be reached with no entropy change if the process is reversible. Also as a mathematical consequence, the entropy maximum principle allows the establishment of the following equations,

$$dS = 0 \quad \text{and} \quad d^2 S < 0 \quad \text{at state 2} \tag{46.6}$$

which then can be used in calculating the nature of the new equilibrium state.

Among the physical consequences, the reversible isentropic process provides a unique limit on process path, which also results in maximal efficiency. Also, the fact that the entropy of real isolated systems always rises provides guidance about which new states may be reached and which may not. Through some operational arguments, but primarily by using statistical mechanics on the molecular level, entropy was shown to be a measure of disorder. This supports the observation that isolated systems undergoing any process become less orderly; mess increases unless an external agent is employed to make order, all consistent with the entropy increase law. Profoundly, entropy is thus regarded to be the scientific indicator of the direction of time — "the arrow of time," after Eddington. The inevitable increase of disorder/entropy with time has led to deeper questions about the origin of the world and indeed of time itself, about the future of the universe in which disorder continuously grows, perhaps to a state of utter disorder (i.e., death), and has raised much philosophical discourse related to these issues. Significant attempts have been made to relate entropy and the second law to almost any human endeavor, including communications, economics, politics, social science, and religion (Bazarov [1964] and Georgescu-Roegen [1971], among many), not always in a scientifically convincing manner.

46.3 The Second Law for Bulk Flow

Based on Equation (46.4), the entropy of a fixed amount of mass (which, by definition, does not give mass to its environment or receive any from it) receiving an amount δQ of heat from a heat reservoir will change as
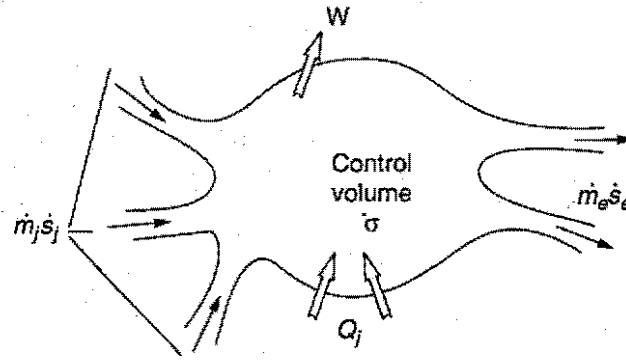
FIGURE 46.5 Entropy accounting for a control volume.

$$dS \geq \frac{\delta Q}{T} \tag{46.7}$$

The amount of entropy produced in the mass due to reversible heat transfer from the reservoir is $\delta Q/T$, and, according to the second law as expressed by Equation (46.4) and Equation (46.5), the amount of entropy produced due to the inevitable internal process irreversibilities, σ, is

$$\sigma \equiv dS - \frac{\delta Q}{T} \geq 0 \tag{46.8}$$

Addressing a transient and more general case, shown in Figure 46.5, the rate of entropy generation due to irreversibilities ($\dot{\sigma}$) in a given control volume that has (1) work, heat (Q), and diffusion (mass transfer) interactions of k species with its environment, and (2) bulk molar flows (N, moles/unit time) incoming (subscript i) and exiting (subscript e), can be expressed by simple entropy accounting as

$$\dot{\sigma} = \frac{dS_{cv}}{dt} - \sum_j \frac{\dot{Q}_j}{T_j} - \sum_i \left(\sum_k \dot{N}_k s_k \right)_i + \sum_e \left(\sum_k \dot{N}_k s_k \right)_e - \sum_k (\dot{N}_{k,e} - \dot{N}_{k,i}) s_{o,k} \geq 0 \tag{46.9}$$

where t is time, ds_{cv}/dt is the rate of entropy accumulation in the control volume, subscript j is the number of heat interactions with the environment, s is the specific molar entropy (entropy per mole), and subscript o refers to the conditions of this environment. Equation (46.9) expresses the fact that the entropy of this control volume changes due to heat interactions with its environment, due to the transport of entropy with entering and exiting bulk and diffusional mass flows, and due to internal irreversibilities (work interactions do not change the entropy).

46.4 Applications

Direction and Feasibility of Processes

Compliance with the second law is one of the criteria applied to examine the feasibility of proposed processes and patents. For example, we will examine such compliance for a steady-state combustion process in which it is proposed that methane preheated to 80°C be burned with 20% excess air preheated to 200°C in a leak-tight well-insulated atmospheric-pressure combustor. Since the combustor is isolated from its environment, compliance with the second law will be inspected by calculating the entropy change in the reaction
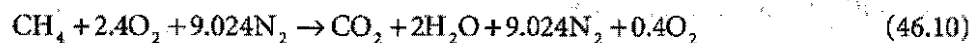
$$CH_4 + 2.4O_2 + 9.024N_2 \rightarrow CO_2 + 2H_2O + 9.024N_2 + 0.4O_2 \tag{46.10}$$

TABLE 46.1 Analysis of a Methane Combustion Reaction

	Moles n_i	$y_i; p_i$ atm	T K	s kJ/kmol · K	s_o kJ/kmol · K	$h_o = h(T_o, p_o)$ kJ/kmol	$h(T, p)$ kJ/kmol	a_{ch} kJ/kmol	a kJ/kmol	$n_i a$ kJ/kmol CH_4
					Reactant					
CH_4	1	0.0805	353	213.5	186.3	−74,900	−72,854	830,745	824,685	824,685
O_2	2.4	0.1932	473	232.6	205.0	0	5309	−129	−3036	−7286
N_2	9.024	0.7263	473	207.8	191.5	0	5135	−102	176	1585
$\Sigma_{reactants}$	12.424	1.0000								818,984
					Product					
CO_2	1	0.0805	2241	316.2	213.7	−393,800	−286,970	13,855	90,140	90,140
O_2	0.4	0.0322	2241	273.1	205.0	0	68,492	−4568	43,639	17,456
N_2	9.024	0.7263	2241	256.1	191.5	0	64,413	−102	45,060	406,623
H_2O (v)	2	0.1610	2241	270.3	188.7	−242,000	−157,790	4138	64,031	128,062
$\Sigma_{products}$	12.424	1.0000								642,281

Note: Dead state: $p_o = 1$ atm, $T_o = 298$ K; atmospheric composition (molar fractions): $N_2 = 0.7567$, $O_2 = 0.2035$, $H_2O = 0.0303$, $CO_2 = 0.0003$.

where it may be noted that the number of moles of air was adjusted to reflect 20% excess air and that the excess oxygen and all of the nitrogen are assumed to emerge from the combustor unreacted. The entropy change can be expressed by using Equation (46.9), which for this problem is reduced to

$$\sigma = \sum_p n_p s_p - \sum_r n_r s_r \qquad (46.11)$$

where the subscripts p and r refer to the reaction products and reactants, respectively, n_i is the number of moles of species i, evident from Equation (46.10), and s_i is the molar entropy of species i, to be found from the literature based on the temperature and partial pressure.

The calculation procedure is outlined in Table 46.1, and further detail can be found in several of the references, such as Howell and Buckius [1992]. The partial pressures of the participating species are easily determined from the molar composition shown in Equation (46.10). The temperature of the reactants is given, and that of the reaction products exiting the combustor, T_p, is calculated from the first law, where the enthalpies of the species, which are primarily dependent on the temperature, are obtained from reference tables or correlations. In this case it is found that $T_p = 2241$ K. Based on this information, the entropies of the species are either found in the literature or calculated from available correlations or gas state equations. The results are listed in Table 46.1, which contains, besides the entropy values, additional information that will be used in another example later.

Application of these results to Equation (46.11) gives

$$\sigma = [1(316.2) + 0.4(273.1) + 9.024(256.1) + 2(270.3)]$$

$$- [1(213.5) + 2.4(232.6) + 9.024(207.8)] \qquad (46.12)$$

$$= 630.2 \text{ kJ} / (\text{kmol} \cdot \text{K}) > 0$$

thus proving compliance of the proposed reaction with the second law and not denying its feasibility. It may be noted that such compliance is a necessary but not always sufficient condition for proving actual process feasibility; additional conditions, such as the existence of a spark in this example, may also be needed.
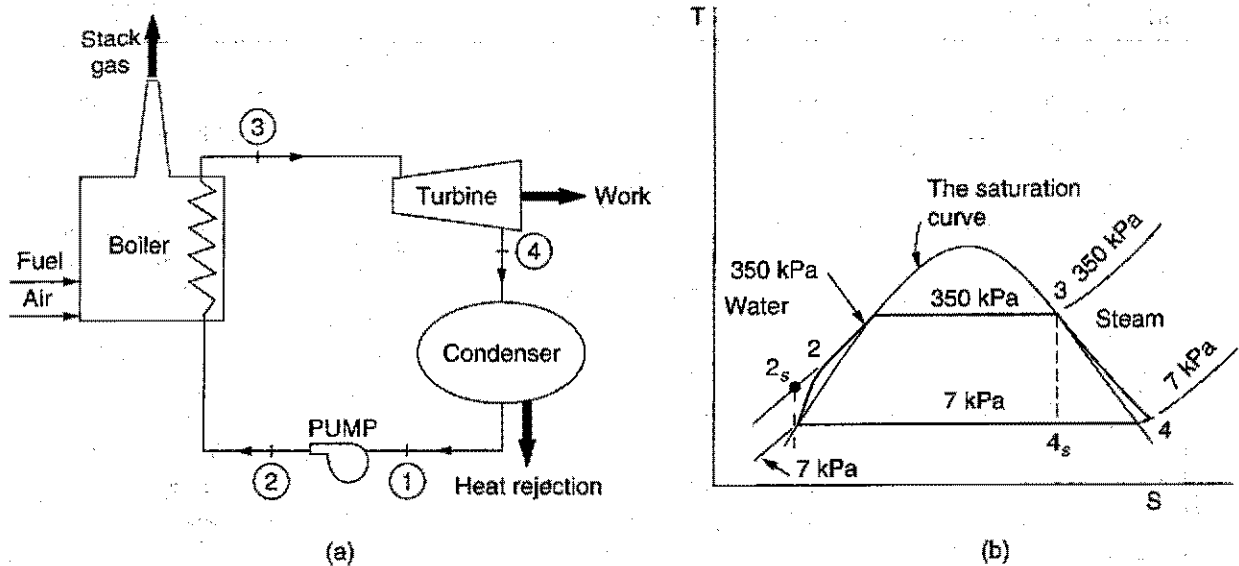
FIGURE 46.6 The Rankine cycle example: (a) the Rankine power cycle; (b) temperature-entropy diagram of the Rankine cycle.

Process Efficiency

Since reversible (isentropic for isolated systems) processes have maximal work-producing efficiency, they are often used as the basis for comparison in the definition of real process efficiencies, defined for work-producing processes (turbines, engines, etc.) as

$$\eta_{is} \equiv \frac{W_p}{W_{p,is}} \tag{46.13}$$

where η_{is} is the so-called "isentropic efficiency," subscript p refers to the work produced, and p, is to the work that would have been produced if the process was isentropic. For work-consuming processes (such as pumps, fans, etc.), the isentropic efficiency is defined as

$$\eta_{is} \equiv \frac{W_{c,is}}{W_c} \tag{46.14}$$

where subscript c refers to the work consumed in the process and c, is to the work that would have been consumed if the process was isentropic.

For example, the isentropic efficiency of the turbine in the simple Rankine cycle shown in Figure 46.6(a) and qualitatively charted on the temperature-entropy (*T-S*) diagram of Figure 46.6(b), in which superheated steam expands from the pressure $p_3 = 350$ kPa to the condenser pressure $p_4 = 7$ kPa, would be calculated using Equation (46.11) as follows. If the expansion from p_3 to p_4 could have been performed isentropically (i.e., reversibly in this case), the turbine would have produced the maximal amount of work, with the expansion of the steam terminating on the intersection points 4_s of the p_4 isobar and the isentrope descending vertically from point 3, with $s_{4_s} = s_3$. Having thus the values of s_{4_s} and p_4 allows the determination of the **enthalpy,** h_{4_s}, shown in Table 46.2 (only the parameters in bold in this table would be addressed in this example). Assuming that the differences between the inlet-to-exit (states 3 and 4 in Figure 46.6) elevations and kinetic energies of the steam are negligible compared to the respective enthalpy difference and that the turbine does not exchange heat with its environment, the isentropic work $W_{p,is}$ can be calculated from the first law equation for the turbine control volume, reduced to

TABLE 46.2 Data for Figure 46.6

State	p, kPa	T, K	s, kj/kg·K	h, kJ/kg	a, kJ/kg	h, kJ/kg fuel	a, kJ/kg fuel
				The Steam/Water Loop			
1	7	312.23	0.5590	163.35	1.36	2260.4	18.8
2$_s$	350	312.23	0.5590	163.70	1.71	2265.3	23.6
2	350	312.38	0.5606	163.87	1.40	2267.6	19.3
3	350	782.75	8.2798	3506.00	1042.05	48,515.7	14,419.8
2$_s$	7	313.15	8.2798	2573.50	109.55	35,611.9	1515.9
4	7	367.25	8.5821	2676.10	122.02	37,031.7	1688.5
				The Fuel, Air, and Stack Gas			
5	101	298.15	HHV = 50,019.00		a_{fuel} = 51,792.00	50,019.0	51,792.0
6	101	298.15	6.6999	299.03	−0.70	6158.1	−14.4
7	101	423.15	7.3388	459.81	79.40	9929.0	1714.5

Note: Dead state: $p_c = 1$ atm, $T_o = 298$ K. Atmospheric composition (molar fractions): $N_2 = 0.7567$, $O_2 = 0.2035$, $H_2O = 0.0303$, $CO_2 = 0.0003$.

$$W_{p,is} = h_3 - h_{4s} \qquad (46.15)$$

In actuality the expansion is irreversible. The second law tells us that the entropy in the process will increase, with the expansion terminating on the same isobar p_4, but at a point 4 where $s_4 > s_3 = s_{4_s}$, which is indeed true in this example, as shown in Table 46.2. The work produced in this process, W_p, is again calculated from the first law:

$$W_p = h_3 - h_4 \qquad (46.16)$$

Using Equation (46.13) and the enthalpy values listed in Table 46.2, the isentropic efficiency in this example is

$$\eta_{is} = \frac{h_3 - h_4}{h_3 - h_{4_s}} = \frac{35060 - 26761}{35060 - 25735} = 0.89 \qquad (46.17)$$

Although not shown here, the data in Figure 46.6 include calculations assuming that the isentropic efficiency of the pump is 0.7. State 2$_s$ in Figure 46.6(b) would have been reached if the pumping process starting from state 1 was isentropic; using Equation (46.14) and the given isentropic efficiency of the pump allows the determination of state 2 attained by the real process (note that states 2$_s$, 2, and 3 are here all on the same 350 kPa isobar), where s_2 is therefore greater than s_1.

Although isentropic efficiencies as defined here have a reasonable rationale and are used widely, important issue has been taken with their fundamental usefulness. Using Figure 46.6(b), it can be argued that a better definition of such efficiency (to be named effectiveness, ε) would be given if the work W_p actually produced, say in the expansion 3–4, $(W_{p,3-4})_{actual}$ [the same as the W_p used in Equation (46.14)], was compared with the work that would have been produced if the expansion from 3 to 4 was reversible $[(W_{p,3-4})_{reversible}]$,

$$\varepsilon = \frac{(W_{p,3-4})_{actual}}{(W_{p,3-4})_{reversible}} \qquad (46.18)$$

rather than comparing it to work that would have been obtained in the isentropic expansion ending at a state 4$_s$, which does not actually exist in the real process. An example of a deficiency of the isentropic

efficiency (η_{is}) compared with the effectiveness (ε) is that it does not give credit to the fact that the steam exiting the turbine at state 4 has a higher temperature than if it had exited at state 4_s, and thus has the potential to perform more work. This is especially poignant when, as usual, additional stages of reheat and expansion are present in the plant. This reasoning and further comments on effectiveness are given in the following section.

Exergy Analysis

Based on the second law statement that only a fraction of heat energy can be converted into work, a very important application of the second law is the analysis of the potential of energy to perform useful work, that is, the examination of the "quality" of energy. To lay the grounds for such analysis, let us address for simplicity a steady flow and state open-flow system such as depicted in Figure 46.5, neglecting any potential and kinetic energy effects. The amount of work produced by the system is from the first law of thermodynamics,

$$W = \sum_i h_i m_i - \sum_e m_e h_e + \sum_j Q_j \qquad (46.19)$$

where h is the specific enthalpy of each incoming or exiting stream of matter m.

As explained earlier, the maximal amount of work would be produced if the process is reversible, in which case entropy generation due to process irreversibilities (σ) is zero (although entropy change of the system due to the heat interactions Q_j at the respective temperatures T_j is nonzero). Multiplying the steady-state form of Equation (46.10) by some constant temperature T (to give it energy units) and subtracting it from Equation (46.19) yields

$$W_{rev} = \left(\sum_i m_i h_i - \sum_e m_e h_e \right) - T\left(\sum_i m_i s_i - \sum_e m_e s_e \right) + \sum_j Q_j \left(1 - \frac{T}{T_j} \right) \qquad (46.20)$$

As can be seen from this equation, the reversible work output in the process $i \rightarrow e$ would be further maximized if the temperature at which the heat interaction occurs, T, would be the lowest practically applicable in the considered system, say T_o, yielding an expression for the maximal work output potential of the system, as

$$W_{max\,i \rightarrow e} = \sum_i m_i (h_i - T_o s_i) - \sum_e m_e (h_e - T_o s_e) + \sum_j Q_j \left(1 - \frac{T_o}{T_j} \right) \qquad (46.21)$$

The term $(h - T_o s)$ appearing at the right side of this equation is thus the measure of a system's potential to perform useful work and therefore of great thermodynamics significance. Composed of thermodynamic properties at a state and of the constant T_o, it is also a thermodynamic property at that state. This term is called the flow *exergy* or flow *availability function, b*:

$$b \equiv h - T_o s \qquad (46.22)$$

Further examination of Equation (46.22) shows that a system at state i would produce the maximal useful work when the new equilibrium state e is identical to the ambient conditions o, since at that state all the driving forces of the system — such as temperature, concentration, and pressure differences — are zero and the system cannot by itself produce any more useful work. The maximal work output, assuming mass conservation, is then

$$W_{max,i \to o} = \sum_i m_i[(h_i - h_o) - T_o(s_i - s_o)] \qquad (46.23)$$

The term $[(h - h_o) - T_o(s - s_o)]$ is also a property and is the measure of a system's potential to perform useful work between any given state and the so-called "dead state," at which the system can undergo no further spontaneous processes. This term is called *flow exergy* or *flow availability, a*:

$$a \equiv (h - h_o) - T_o(s - s_o) \qquad (46.24)$$

Since enthalpy is the measure of the energy in flow systems, examination of Equation (46.21) through Equation (46.24) shows clearly that the portion of the energy h that cannot be converted to useful work is the product $T_o s$.

The last term on the right side of Equation (46.21) is the exergy of the heat sources Q_j, at the respective temperatures T_j, exchanging heat with the considered thermodynamic system. The form of this term is the Carnot cycle work output between T_j and the dead state temperature T_o, which indeed would produce the maximal work and is thus also the exergy of these heat sources by definition. Shaft and other mechanical power, and electric power, are pure exergy.

Turning now to real, irreversible steady state processes, their exergy accounting equation — developed using Equation (46.9), Equation (46.21), and Equation (46.24) — is

$$W = \sum_j Q_j \left(1 - \frac{T_o}{T_j}\right) + \sum_i m_i a_i - \sum_e m_e a_e - T_o \sigma \qquad (46.25)$$

where the work output of the process in this control volume is, in the order of terms on the right side of the equation, produced due to (1) heat interactions Q_j at the respective temperatures T_j, with the control volume, and (2) and (3) the difference between the exergies flowing in and exiting the control volume, and is diminished by (4) the entropy generation due to process irreversibilities. This last term, $T_o \sigma$, amounts to the difference between the maximal work that could have been produced in a reversible process [Equation (46.21) and Equation (46.24)] and the amount produced in the actual irreversible process [Equation (46.25)]. It is called the *irreversibility* (*I*) or *lost work* of the process.

Beyond exergy changes due to temperature and pressure driving forces, multicomponent systems also experience exergy changes due to component mixing, phase change, and chemical reactions. It was found convenient to separate the exergy expression into its "physical" (a_{ph}) and "chemical" (a_{ch}) constituents,

$$a = a_{ph} + a_{ch} \qquad (46.26)$$

where the *physical exergy* is the maximal work obtainable in a reversible physical process by a system initially at T and p and finally at the dead state T_o, p_o, and the *chemical exergy* is the maximal work obtainable from a system at dead state conditions T_o, p_o, initially at some species composition and finally at the dead state composition (such as the datum level composition of the environment). The total flow exergy, showing the thermal, mechanical, and chemical flow exergy components (segregated by the double brackets) is

$$a = [[(h - h_o) - T_o(s - s_o)]](\text{thermal}) + \left[\left[\frac{\mathbf{v}^2}{2} + gz\right]\right] (\text{mechanical})$$

$$\qquad (46.27)$$

$$+ \left[\left[\sum_k x_k(\mu_k^o - \mu_{o,k})\right]\right] (\text{chemical})$$

where v is the flow velocity, g is the gravitational acceleration, z is the flow elevation above a zero reference level, x_k is the molar fraction of species k in the mixture, μ_k^o is the **chemical potential** of species k at T_o and p_o, and $\mu_{k,o}$ is the chemical potential of species k at the system dead state defined by T_o, p_o, and the dead state composition.

The general transient exergy accounting equation that includes both physical and chemical exergy is

$$\frac{dA_{cv}}{dt}\text{(rate of exergy storage)} = \sum_j\left(1-\frac{T_o}{T_j}\right)\dot{Q}_j - \left(\dot{W}_{cv} - p_o\frac{dV_{cv}}{dt}\right) + \sum_i \dot{m}_i a_i$$

$$- \sum_e \dot{m}_e a_e \text{(rates of exergy transfer)} \qquad (46.28)$$

$$- \dot{I}_{cv}\text{(rate of exergy destruction)}$$

where A_{cv} is the exergy of the control volume, $\dot{W}_{cv}$ is the work performed by the control volume, $p_o\,(dV_{cv}/dt)$ is the work due to the transient volume change of the control volume, a_i and a_e are the total flow exergies composed of both the physical and chemical components, and $\dot{I}_{cv}$ ($\equiv T_o\dot{\sigma}$) is the irreversibility, that is, the rate of exergy destruction. A more detailed breakdown of exergy, in differential equation form, is given in Dunbar et al. [1992].

For a *closed system* (i.e., one that does not exchange mass with its environment but can have work and heat interactions with it) at a state defined by the specific internal energy u, specific volume v, and specific entropy s, the expression for the exergy, a^o, is

$$a^o = \left(u + \frac{v^2}{2} + gz - u_o\right) + p_o(v - v_o) - T_o(s - s_o) \qquad (46.29)$$

Selection of the dead state for evaluating exergy is based on the specific application considered. Thus, for example, the dead state for the analysis of a water-cooled power plant operating at a certain geographic location should consist of the cooling water temperature and the ambient atmospheric pressure and composition, all at that location. Much work has been performed in defining "universal" dead states for processes and materials [Szargut et al., 1988].

Example — Exergy Analysis of a Power Plant

To demonstrate the calculation procedure and the benefits of exergy analysis, we will perform such an analysis on the simple Rankine cycle described in Figure 46.6. The fuel used in the boiler is methane, undergoing the same combustion reaction as described in Equation (46.10). Both fuel and air enter the boiler at 25°C, 1 atm, and the combustion products exit the stack at 150°C.

Addressing the steam/water (single component) Rankine cycle loop first, the values of p, T, s, and h are already available from the example given and are listed in Table 46.2. Given the dead state conditions listed under the table, the flow exergy (a) per kg of the water and steam is calculated from Equation (46.24) and listed in the table column to the left of the vertical dividing line.

The three bottom rows of the table list the properties of the inflowing fuel and air and of the stack exhaust gas. The enthalpy of the fuel is its higher heating value (HHV), which, along with exergy, is obtained from fuel property tables [Szargut et al., 1988; Howell and Buckius, 1992; Moran and Shapiro, 1992]. The specific flow exergy values of the air and stack gas are calculated from Equation (46.28) (with negligible kinetic and potential energy components) and listed to the left of the vertical dividing line.

It is sensible to analyze the power system based on the fuel energy and exergy input, in other words, to determine how this fuel input is distributed among the different system components and pro-
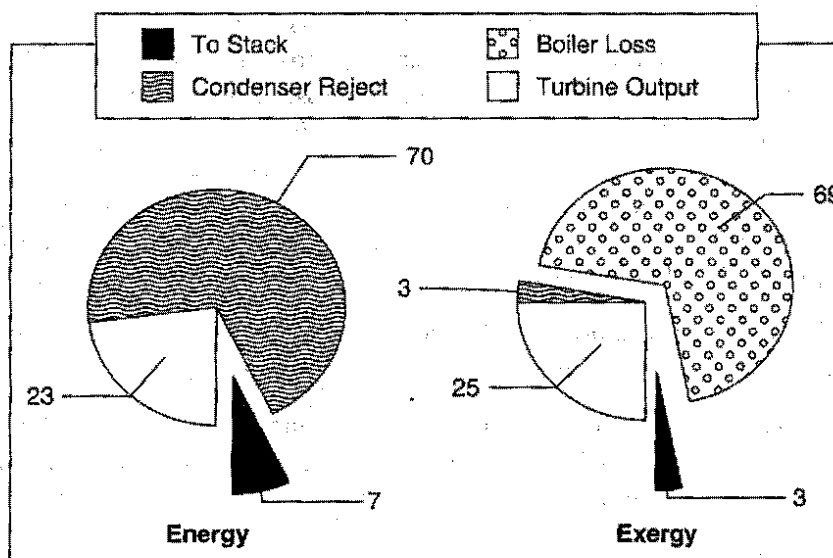
FIGURE 46.7 Energy and exergy breakdown for the Rankine power cycle example.

cesses. To that end we determine, per unit mass of fuel, the mass of cycle steam [here found to be 13.8 (kg steam)/(kg fuel) by applying the energy conservation equation to the boiler] and the mass of air and stack gas [20.6 (kg air)/(kg fuel) and 21.6 (kg exhaust gas)/(kg fuel) by applying Equation (46.10)]. These results are listed in the last two columns of the table.

Examination of the results is encouraged, and some of the most important ones, which describe the fuel energy and exergy distribution among the different system components/processes, are shown in Figure 46.7 *Energy* analysis indicates that the major energy loss, 70%, is due to the heat rejected in the condenser. Examination of the *exergy* analysis chart shows, however, that this large energy loss amounts to only 3% of the fuel exergy, and even complete elimination of the condenser heat rejection (if it were at all feasible) would increase the cycle efficiency by only three percentage points. Of course, this is because the heat rejected in the condenser is at a low temperature, only slightly elevated above that of the ambient, and thus has commensurately little potential to perform work despite its large energy. Another very significant difference is the fact that the exergy analysis identifies the major losses, 69%, to be in the boiler, due to the combustion and gas-to-steam/water heat transfer processes, whereas the energy analysis associates no loss to these processes. Finally, the exergy analysis attributes much less loss to the stack gas than the energy analysis does. Notably, the turbine output has almost the same percentage in both analyses, which is because the output is shaft power (i.e., pure exergy), and the HHV and exergy of the fuel are nearly identical. In conclusion, it is only exergy analysis that can correctly identify and evaluate the losses (irreversibilities) that diminish the ability of processes to perform useful work.

Example — Exergy Analysis of a Combustion Process

The methane combustor analyzed earlier, for which the data are given in Table 46.1, has a 100% energy efficiency because its enclosure is adiabatic and impermeable, as can also be ascertained by performing a first law energy conservation check using the data in Table 46.1. The intuitive implication of this result is that the combustor is thus perhaps "ideal" and requires no further technological improvement. It is interesting therefore to examine the effect that it has on the potential of the invested consumables (i.e., the fuel and other reactants) on producing useful work. The flow exergy a and the chemical exergy a_{ch} are calculated by using Equation (46.27), and property values from gas tables or correlations given in the literature, with the dead state (including the atmospheric composition) described at the bottom of Table 46.1. The calculation results are summarized in Table 46.1, showing, first, that the total exergy of the combustion products (642 281 kJ/mmol CH_4) is

only 78.4% of the original exergy of the reactants (818 984 kJ/kmol CH_4) that they possessed prior to combustion. This combustion process, although ideal from the energy standpoint, destroyed 21.6% of the original exergy. Practical combustion processes destroy even more exergy and are typically the largest cause for the lost work (irreversibility) in current-day fossil fuel power plants. Whereas energy (first law) analysis identified this process as "ideal," exergy analysis was unique in its ability to recognize and quantify this power production efficiency loss, which we can subsequently attempt to reduce. More information on this approach and the reasons for combustion irreversibility can be found in Dunbar and Lior [1994].

Examination of Table 46.1 also shows that the exergy of the fuel is dominant among the reactants and that the chemical exergy, a_{ch}, is small relative to the overall exergy.

These examples have clearly demonstrated the unique role and importance of second law analysis. Integration of such analysis with conventional first law (energy) analysis is necessary and increasingly seen in practice [cf. Bejan, 1988; Moran and Shapiro, 1992].

Defining Terms

Adiabatic — A process or surface allowing only work interactions. Since most introductory thermodynamics texts consider only work and heat interactions, *adiabatic* is most often interpreted as a process or surface allowing no heat interactions.

Chemical potential — A potential given by $\mu_k \equiv h_k - Ts_k$, where h_k and s_k are, respectively, the enthalpy and entropy of the species k, and T is the temperature.

Cycle — A series of processes that bring a thermodynamic system back to its original state.

Enthalpy — Given by $h \equiv u + pv$, where u is the internal energy, p is the pressure, and v is the specific volume.

Environment — The environment of a thermodynamic system consists of everything outside of that system that could conceivably have some influence on it.

Equilibrium — A state in which all of the properties of a system that is not subjected to interactions do not change with time. Equilibrium states may be of various types: stable, neutral, metastable, and unstable.

Heat reservoir — A system in a stable equilibrium state such that, when subjected to finite heat interactions, its temperature remains constant. Although this is just a concept for simplifying the exposition of thermodynamics, the atmosphere, oceans, lakes, and rivers were often considered as practical examples of such a reservoir. It is noteworthy that the large and ever-increasing magnitudes of human-made heat interactions with these natural elements now invalidate their definition as "heat reservoirs" in this thermodynamic sense, because these interactions in fact change their temperature and cause increasingly adverse environmental effects.

Stable state — A system is in a stable state (or stable equilibrium state) if a finite change of state of the system cannot occur without leaving a corresponding finite change in the state of the environment. In other words a finite external influence would be needed to budge a system out of its stable state; small natural pulses and fluctuations would not suffice.

State — The state of a thermodynamic system is defined by all of the properties of the system, such as pressure, temperature, volume, composition, and so forth. A system returns to the same state when all the properties attain their original values.

Thermodynamic system — A thermodynamic system is whatever we enclose for the purpose of a study by a well-defined surface, which may be either material or imaginary and which can be isolated from everything else (i.e., from the "environment").

References

Bazarov, I. P. 1964. *Thermodynamics*, Pergamon Press, Oxford, England.

Bejan, A. 1988. *Advanced Engineering Thermodynamics,* John Wiley & Sons, New York.

Callen, H. B. 1985. *Thermodynamics and an Introduction to Thermostatistics,* 2nd ed. John Wiley & Sons, New York.

Dunbar, W. R., Lior, N., and Gaggioli, R. 1992. The component equations of energy and exergy. *ASME J. Energy Resour. Technol.* (114):75–83.

Dunbar, W. R. and Lior, N. 1994. Sources of combustion irreversibility. *Comb. Sci. Technol.* 103:41–61.

Georgescu-Roegen, N. 1971. *The Entropy Law and the Economic Process,* Harvard University Press, Cambridge, MA.

Hatsopoulos, G. N. and Keenan, J. H. 1965. *Principles of General Thermodynamics,* John Wiley & Sons, New York.

Howell, J. R. and Buckius, R. O. 1992. *Fundamentals of Engineering Thermodynamics,* McGraw-Hill, New York.

Moran, M. J. and Shapiro, H. N. 1992. *Fundamentals of Engineering Thermodynamics,* John Wiley & Sons, New York.

Stull, D. R. and Prophet, H. 1971. *JANAF Thermochemical Tables,* 2nd ed. NSRDS-NBS 37. National Bureau of Standards, Washington, DC.

Szargut, J., Morris, D. R., and Steward, F. R. 1988. *Exergy Analysis of Thermal, Chemical and Metallurgical Processes,* Hemisphere, New York.

Further Information

Anderson, E. E. *Thermodynamics,* 1994. PWS, Boston, MA. Integrates first and second law analysis.

Sonntag, R. E. and Van Wylen, G. J. *Introduction to Thermodynamics Classical and Statistical,* John Wiley & Sons, New York. Widely used textbook.