

Chapter 2

The First and Second Laws of Thermodynamics

2.1 Introduction

A conventional thermodynamic analysis involves an application of the first law of thermodynamics, also known as energy analysis. Exergy analysis is a thermodynamic analysis technique based on the second law of thermodynamics that provides an alternative and illuminating means of assessing and comparing processes and systems rationally and meaningfully. In particular, exergy analysis yields efficiencies that provide a true measure of how nearly actual performance approaches the ideal, and identifies more clearly than energy analysis the causes and locations of thermodynamic losses and the impact of the built environment on the natural environment. Consequently, exergy analysis can assist in improving and optimizing designs.

Energy and exergy efficiencies are considered by many to be useful for the assessment of energy conversion and other systems and for efficiency improvement. By considering both of these efficiencies, the quality and quantity of the energy used to achieve a given objective is considered and the degree to which efficient and effective use of energy resources is achieved can be understood. Improving efficiencies of energy systems is an important challenge for meeting energy policy objectives. Reductions in energy use can assist in attaining energy security objectives. Also, efficient energy utilization and the introduction of renewable energy technologies can significantly help solve environmental issues. Increased energy efficiency benefits the environment by avoiding energy use and the corresponding resource consumption and pollution generation. From an economic as well as an environmental perspective, improved energy efficiency has great potential [2].

An engineer designing a system is often expected to aim for the highest reasonable technical efficiency at the lowest cost under the prevailing technical, economic, and legal conditions, and with regard to ethical, ecological, and social consequences. Exergy methods can assist in such activities and offer unique insights into possible improvements with special emphasis on environment and

sustainability. Exergy analysis is a useful tool for addressing the environmental impact of energy resource utilization, and for furthering the goal of more efficient energy-resource use, for it enables the locations, types, and true magnitudes of losses to be determined. Also, exergy analysis reveals whether and by how much it is possible to design more efficient energy systems by reducing inefficiencies.

2.2 Energy Change and Energy Transfer

Energy is the capacity for doing work. The energy of a system consists of internal, kinetic, and potential energies. Internal energy consists of thermal (sensible and latent), chemical, and nuclear energies. Unless there is a chemical or nuclear reaction the internal change of a system is due to thermal energy change. In the absence of electric, magnetic, and surface tension effects, among others, the total energy change of a system is expressed as

$$\Delta E = E_2 - E_1 = \Delta U + \Delta KE + \Delta PE \quad (2.1)$$

where internal, kinetic, and potential energy changes are

$$\Delta U = m(u_2 - u_1) \quad (2.2)$$

$$\Delta KE = \frac{1}{2}m(V_2^2 - V_1^2) \quad (2.3)$$

$$\Delta PE = \frac{1}{2}mg(z_2 - z_1) \quad (2.4)$$

For most cases, the kinetic and potential energies do not change during a process and the energy change is due to the internal energy change:

$$\Delta E = \Delta U = m(u_2 - u_1) \quad (2.5)$$

Energy has the unit of kJ or Btu (1 kJ = 0.94782 Btu). Energy per unit of time is the rate of energy and is expressed as

$$\dot{E} = \frac{E}{\Delta t} \text{ (kW or Btu/h)} \quad (2.6)$$

The energy rate unit is kJ/s, which is equivalent to kW or Btu/h (1 kW = 3412.14 Btu/h). Energy per unit mass is called specific energy; it has the unit of kJ/kg or Btu/lbm (1 kJ/kg = 0.430 Btu/lbm).

$$e = \frac{E}{m} \text{ (kJ/kg or Btu/lbm)} \quad (2.7)$$

Energy can be transferred to or from a system in three forms: mass, heat, and work. They are briefly described below.

2.2.1 Mass Transfer

The mass entering a system carries energy with it and the energy of the system increases. The mass leaving a system decreases the energy content of the system. When a fluid flows into a system at a mass flow rate of \dot{m} (kg/s), the rate of energy entering is equal to mass times energy of a unit mass of a flowing fluid: $\dot{m}(h + V^2/2 + gz)$ (kW), where $h = u + Pv$ and Pv is the flow energy (also called flow work) described below.

2.2.2 Heat Transfer

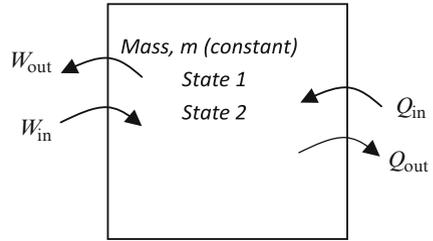
The definitive experiment which showed that heat was a form of energy convertible into other forms was carried out by the Scottish physicist James Joule. Heat is the thermal form of energy and heat transfer takes place when a temperature difference exists within a medium or between different media. Heat always requires a difference in temperature for its transfer. Higher temperature differences provide higher heat transfer rates.

Heat transfer has the same unit as energy. The symbol for heat transfer is Q (kJ). Heat transfer per unit mass is denoted by q (kJ/kg). Heat transfer per unit time is the rate of heat transfer \dot{Q} (kW). If there is no heat transfer involved in a process, it is called an *adiabatic process*.

2.2.3 Work

Work is the energy that is transferred by a difference in pressure or under the effect of a force of any kind and is subdivided into shaft work and flow work. Work is denoted by W . Shaft work is mechanical energy used to drive a mechanism such as a pump, compressor, or turbine. Flow work is the energy transferred into a system by fluid flowing into, or out of, the system. The rate of work transfer per unit time is called *power* \dot{W} (kW). Work has the same unit as energy. The direction of heat and work interactions can be expressed by sign conventions or using subscripts such as “in” and “out”.

Fig. 2.1 A general closed system with heat and work interactions



2.3 The First Law of Thermodynamics

So far, we have considered various forms of energy such as heat Q , work W , and total energy E individually, and no attempt has been made to relate them to each other during a process. The first law of thermodynamics, also known as the conservation of energy principle, provides a sound basis for studying the relationships among the various forms of energy and energy interactions.

Based on experimental observations, the first law of thermodynamics states that energy can be neither created nor destroyed during a process; it can only change forms. Therefore, every bit of energy should be accounted for during a process. We all know that a rock at some elevation possesses some potential energy, and part of this potential energy is converted to kinetic energy as the rock falls. Experimental data show that the decrease in potential energy (mgz) exactly equals the increase in kinetic energy when the air resistance is negligible, thus confirming the conservation of energy principle for mechanical energy [1].

The first law of thermodynamics can be expressed for a general system inasmuch as the net change in the total energy of a system during a process is equal to the difference between the total energy entering and the total energy leaving the system:

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}} \quad (2.8)$$

In rate form,

$$\dot{E}_{\text{in}} - \dot{E}_{\text{out}} = \frac{dE}{dt} \quad (2.9)$$

For a closed system undergoing a process between initial and final states (states 1 and 2) with heat and work interactions with the surroundings (Fig. 2.1):

$$\begin{aligned} E_{\text{in}} - E_{\text{out}} &= \Delta E_{\text{system}} \\ (Q_{\text{in}} + W_{\text{in}}) - (Q_{\text{out}} + W_{\text{out}}) &= \Delta U + \Delta \text{KE} + \Delta \text{PE} \end{aligned} \quad (2.10)$$

Fig. 2.2 A general steady-flow control volume with mass, heat, and work interactions

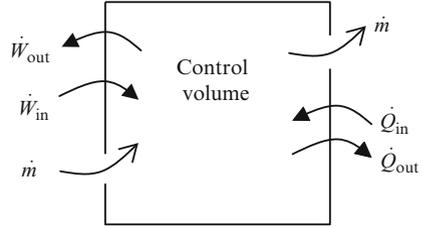
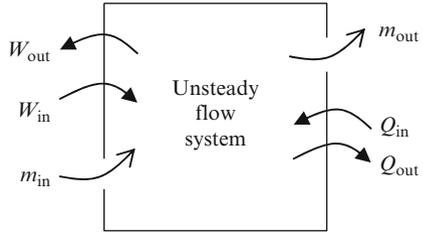


Fig. 2.3 A general unsteady-flow process with mass, heat, and work interactions



If there is no change in kinetic and potential energies:

$$(Q_{in} + W_{in}) - (Q_{out} + W_{out}) = \Delta U = m(u_2 - u_1) \tag{2.11}$$

Let us consider a control volume involving a steady-flow process. Mass is entering and leaving the system and there are heat and work interactions with the surroundings (Fig. 2.2). During a steady-flow process, the total mass and energy content of the control volume remains constant, and thus the total energy change of the system is zero. Then the first law of thermodynamics can be expressed through the balance equation as

$$\begin{aligned} \dot{E}_{in} - \dot{E}_{out} &= \frac{dE}{dt} = 0 \\ \dot{E}_{in} &= \dot{E}_{out} \\ \dot{Q}_{in} + \dot{W}_{in} + \dot{m} \left(h_{in} + \frac{V_{in}^2}{2} + gz_{in} \right) &= \dot{Q}_{out} + \dot{W}_{out} + \dot{m} \left(h_{out} + \frac{V_{out}^2}{2} + gz_{out} \right) \end{aligned} \tag{2.12}$$

If the changes in kinetic and potential energies are negligible, it results in

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m}h_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m}h_{out} \tag{2.13}$$

Charging and discharging processes may be modeled as unsteady-flow processes. Consider an unsteady-flow process as shown in Fig. 2.3. Assuming uniform flow conditions, the mass and energy balance relations may be expressed as

$$m_{in} - m_{out} = m_2 - m_1 \tag{2.14}$$

$$\begin{aligned}
 E_{\text{in}} - E_{\text{out}} &= \Delta E_{\text{system}} \\
 Q_{\text{in}} + W_{\text{in}} + m_{\text{in}} \left(h_{\text{in}} + \frac{V_{\text{in}}^2}{2} + gz_{\text{in}} \right) - Q_{\text{out}} - W_{\text{out}} \\
 - m_{\text{out}} \left(h_{\text{out}} + \frac{V_{\text{out}}^2}{2} + gz_{\text{out}} \right) &= m_2 u_2 - m_1 u_1
 \end{aligned} \tag{2.15}$$

2.4 The Second Law of Thermodynamics

Energy is a conserved property, and no process is known to have taken place in violation of the first law of thermodynamics. Therefore, it is reasonable to conclude that a process must satisfy the first law to occur. However, as explained here, satisfying the first law alone does not ensure that the process will actually take place.

It is common experience that a cup of hot coffee left in a cooler room eventually loses heat. This process satisfies the first law of thermodynamics because the amount of energy lost by the coffee is equal to the amount gained by the surrounding air. Now let us consider the reverse process: the hot coffee getting even hotter in a cooler room as a result of heat transfer from the room air. We all know that this process never takes place. Yet, doing so would not violate the first law as long as the amount of energy lost by the air is equal to the amount gained by the coffee.

As another familiar example, consider the heating of a room by the passage of electric current through a resistor. Again, the first law dictates that the amount of electric energy supplied to the resistance wires be equal to the amount of energy transferred to the room air as heat. Now let us attempt to reverse this process. It will come as no surprise that transferring some heat to the wires does not cause an equivalent amount of electric energy to be generated in the wires.

Finally, consider a paddle-wheel mechanism that is operated by the fall of a mass. The paddle wheel rotates as the mass falls and stirs a fluid within an insulated container. As a result, the potential energy of the mass decreases, and the internal energy of the fluid increases in accordance with the conservation of energy principle. However, the reverse process, raising the mass by transferring heat from the fluid to the paddle wheel, does not occur in nature, although doing so would not violate the first law of thermodynamics.

It is clear from these arguments that processes advance in a certain direction and not in the reverse direction. The first law places no restriction on the direction of a process, but satisfying the first law does not ensure that the process can actually occur. This inadequacy of the first law to identify whether a process can take place is remedied by introducing another general principle, the second law of thermodynamics. We show later in this chapter that the reverse processes discussed above violate the second law of thermodynamics. This violation is easily detected with the help of a property called *entropy*. A process cannot occur unless it satisfies both the first and the second laws of thermodynamics.

The use of the second law of thermodynamics is not limited to identifying the direction of processes. The second law also asserts that energy has quality as well as quantity. The first law is concerned with the quantity of energy and the

transformations of energy from one form to another with no regard to its quality. Preserving the quality of energy is of major concern to engineers, and the second law provides the necessary means to determine the quality as well as the degree of degradation of energy during a process. As discussed later in this chapter, more of high-temperature energy can be converted to work, and thus it has a higher quality than the same amount of energy at a lower temperature.

The second law of thermodynamics is also used in determining the theoretical limits for the performance of commonly used engineering systems such as heat engines and refrigerators, as well as predicting the degree of completion of chemical reactions. The second law is also closely associated with the concept of perfection. In fact, the second law defines perfection for thermodynamic processes. It can be used to quantify the level of perfection of a process, and point out the direction to eliminate imperfections effectively.

Energy has quality as well as quantity. More of the high-temperature thermal energy can be converted to work. Therefore, it results in “the higher the temperature is, the higher the quality of the energy.” Large quantities of solar energy, for example, can be stored in large bodies of water called solar ponds at about 350 K. This stored energy can then be supplied to a heat engine to produce work (electricity). However, the efficiency of solar pond power plants is very low (under 5%) because of the low quality of the energy stored in the source, and the construction and maintenance costs are relatively high. Therefore, they are not competitive even though the energy supply of such plants is free. The temperature (and thus the quality) of the solar energy stored could be raised by utilizing concentrating collectors, but the equipment cost in that case becomes very high.

Work is a more valuable form of energy than heat inasmuch as 100% of work can be converted to heat, but only a fraction of heat can be converted to work. When heat is transferred from a high-temperature body to a lower temperature one, it is degraded because less of it can now be converted to work. For example, if 100 kJ of heat are transferred from a body at 1,000 K to a body at 300 K, at the end we will have 100 kJ of thermal energy stored at 300 K, which has no practical value. But if this conversion were made through a heat engine, up to $1 - 300/1000 = 0.70 = 70\%$ of it could be converted to work, which is a more valuable form of energy. Thus 70 kJ of work potential is wasted as a result of this heat transfer, and energy is degraded [1].

There are numerous forms of second law statements. Two classical statements are as follows.

The Kelvin–Planck statement: It is impossible to construct a device, operating in a cycle (e.g., heat engine), that accomplishes only the extraction of heat energy from some source and its complete conversion to work. This simply shows the impossibility of having a heat engine with a thermal efficiency of 100%.

The Clausius statement: It is impossible to construct a device, operating in a cycle (e.g., refrigerator and heat pump), that transfers heat from the low-temperature side (cooler) to the high-temperature side (hotter), and producing no other effect.

2.5 Entropy

The second law of thermodynamics often leads to expressions that involve inequalities. An irreversible (i.e., actual) heat engine, for example, is less efficient than a reversible one operating between the same two thermal energy reservoirs. Likewise, an irreversible refrigerator or a heat pump has a lower coefficient of performance (COP) than a reversible one operating between the same temperature limits. Another important inequality that has major consequences in thermodynamics is the *Clausius inequality*. It was first stated by the German physicist R.J.E. Clausius (1822–1888), one of the founders of thermodynamics, and is expressed as

$$\oint \frac{\delta Q}{T} \leq 0 \quad (2.16)$$

That is, the cyclic integral of $\delta Q/T$ is always less than or equal to zero. This inequality is valid for all cycles, reversible or irreversible.

Clausius realized in 1865 that he had discovered a new thermodynamic property, and he chose to name this property *entropy*. It is designated S and is defined as

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{int rev}} \quad (2.17)$$

Entropy is an extensive property of a system and is sometimes referred to as *total entropy*. Entropy per unit mass, designated s , is an intensive property and has the unit $\text{kJ/kg} \cdot \text{K}$. The term *entropy* is generally used to refer to both total entropy and entropy per unit mass because the context usually clarifies which one is meant.

The entropy change of a system during a process can be determined by integrating (2.17) between the initial and the final states:

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{int rev}} \quad (2.18)$$

Note that entropy is a property, and like all other properties, it has fixed values at fixed states. Therefore, the entropy change between two specified states is the same no matter what path, reversible or irreversible, is followed during a process.

Consider a cycle made up of two processes: process 1-2, which is arbitrary (reversible or irreversible), and process 2-1, which is internally reversible. From the Clausius inequality it becomes

$$\int_1^2 \left(\frac{\delta Q}{T} \right) + \int_2^1 \left(\frac{\delta Q}{T} \right)_{\text{int rev}} \leq 0 \quad (2.19)$$

The second integral in the previous relation is recognized as the entropy change $S_1 - S_2$. Therefore,

$$\int_1^2 \left(\frac{\delta Q}{T} \right) + S_1 - S_2 \leq 0 \quad (2.20)$$

which can be rearranged as

$$S_2 - S_1 \geq \int_1^2 \left(\frac{\delta Q}{T} \right) \quad (2.21)$$

The inequality sign in the preceding relations is a constant reminder that the entropy change of a closed system during an irreversible process is always greater than the entropy transfer. That is, some entropy is generated or created during an irreversible process, and this generation is due entirely to the presence of irreversibilities. The entropy generated during a process is called *entropy generation* and is denoted by S_{gen} . Noting that the difference between the entropy change of a closed system and the entropy transfer is equal to entropy generation, (2.21) can be rewritten as an equality as

$$\Delta S_{\text{sys}} = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right) + S_{\text{gen}} \quad (2.22)$$

Note that the entropy generation S_{gen} is always a positive quantity or zero. Its value depends on the process, and thus it is not a property of the system. Also, in the absence of any entropy transfer, the entropy change of a system is equal to the entropy generation.

Equation 2.22 has far-reaching implications in thermodynamics. For an isolated system (or simply an adiabatic closed system), the heat transfer is zero, and (2.21) reduces to

$$\Delta S_{\text{isolated}} \geq 0 \quad (2.23)$$

This equation can be expressed as the entropy of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant. In other words, it never decreases. This is known as the *increase of entropy principle*. Note that in the absence of any heat transfer, entropy change is due to irreversibilities only, and their effect is always to increase entropy.

Entropy is an extensive property, thus the total entropy of a system is equal to the sum of the entropies of the parts of the system. An isolated system may consist of any number of subsystems. A system and its surroundings, for example, constitute an isolated system inasmuch as both can be enclosed by a sufficiently large arbitrary boundary across which there is no heat, work, or mass transfer. Therefore, a system and its surroundings can be viewed as the two subsystems of an isolated system, and

the entropy change of this isolated system during a process is the sum of the entropy changes of the system and its surroundings, which is equal to the entropy generation because an isolated system involves no entropy transfer. That is,

$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \quad (2.24)$$

where the equality holds for reversible processes and the inequality for irreversible ones. Note that ΔS_{surr} refers to the change in the entropy of the surroundings as a result of the occurrence of the process under consideration. No actual process is truly reversible, and so we can conclude that some entropy is generated during a process, and therefore the entropy of the universe, which can be considered to be an isolated system, is continuously increasing. The more irreversible a process is, the larger the entropy generated during that process. No entropy is generated during reversible processes.

The increase of the entropy principle does not imply that the entropy of a system cannot decrease. The entropy change of a system can be negative during a process, but entropy generation cannot. The performance of engineering systems is degraded by the presence of irreversibilities, and entropy generation is a measure of the magnitudes of the irreversibilities present during that process. The greater the extent of irreversibilities is, the greater the entropy generation. Therefore, entropy generation can be used as a quantitative measure of irreversibilities associated with a process. It is also used to establish criteria for the performance of engineering devices.

2.5.1 Entropy Balance

The entropy property is a measure of molecular disorder or randomness of a system, and the second law of thermodynamics states that entropy can be created but it cannot be destroyed. Therefore, the entropy change of a system during a process is greater than the entropy transfer by an amount equal to the entropy generated during the process within the system, and the increase of entropy principle for any system is expressed as

$$S_{\text{in}} - S_{\text{out}} + S_{\text{gen}} = \Delta S_{\text{system}} \quad (2.25)$$

This relation is often referred to as the *entropy balance* and is applicable to any system undergoing any process. The entropy balance relation above can be stated as the entropy change of a system during a process is equal to the net entropy transfer through the system boundary and the entropy generated within the system.

Entropy can be transferred by heat and mass. Entropy transfer by heat is expressed as

$$S_{\text{heat}} = \frac{Q}{T} \quad (2.26)$$

Entropy transfer by mass is given by

$$S_{\text{mass}} = ms \quad (2.27)$$

When two systems are in contact, the entropy transfer from the warmer system is equal to the entropy transfer into the cooler one at the point of contact. That is, no entropy can be created or destroyed at the boundary because the boundary has no thickness and occupies no volume. Note that work is entropy-free, and no entropy is transferred by work. The entropy balance in (2.25) can be expressed in the rate form as

$$\dot{S}_{\text{in}} - \dot{S}_{\text{out}} + \dot{S}_{\text{gen}} = dS_{\text{system}}/dt \quad (2.28)$$

Let us reconsider the closed system in Fig. 2.1. The entropy balance on this closed system may be written as

$$\left(\frac{Q}{T}\right)_{\text{in}} - \left(\frac{Q}{T}\right)_{\text{out}} + S_{\text{gen}} = m(s_2 - s_1) \quad (2.29)$$

Now, consider the control volume in Fig. 2.2 with a steady-flow process. The entropy balance on this control volume may be expressed as

$$\left(\frac{\dot{Q}}{T}\right)_{\text{in}} + \dot{m}s_{\text{in}} - \left(\frac{\dot{Q}}{T}\right)_{\text{out}} - \dot{m}s_{\text{out}} + \dot{S}_{\text{gen}} = 0 \quad (2.30)$$

In these equations T represents the temperature of the boundary at which heat transfer takes place. If the system is selected such that it includes the immediate surroundings, the boundary temperature becomes the temperature of the surroundings. Then one can use the surrounding ambient temperature in these equations. For the unsteady-flow process shown in Fig. 2.3, the entropy balance can be expressed as

$$\left(\frac{Q}{T}\right)_{\text{in}} + m_{\text{in}}s_{\text{in}} - \left(\frac{Q}{T}\right)_{\text{out}} - m_{\text{out}}s_{\text{out}} + S_{\text{gen}} = m_2s_2 - m_1s_1 \quad (2.31)$$

In recent decades, much effort has been spent in minimizing the entropy generation (irreversibility) in thermodynamic systems and applications [8].

2.6 Exergy

The attempts to quantify the quality or “work potential” of energy in the light of the second law of thermodynamics has resulted in the definition of the exergy property.

Exergy analysis is a thermodynamic analysis technique based on the second law of thermodynamics that provides an alternative and illuminating means of assessing

and comparing processes and systems rationally and meaningfully. In particular, exergy analysis yields efficiencies that provide a true measure of how nearly actual performance approaches the ideal, and identifies more clearly than energy analysis the causes and locations of thermodynamic losses and the impact of the built environment on the natural environment. Consequently, exergy analysis can assist in improving and optimizing designs. Various books have been written on exergy analysis and applications [5, 8–11].

Energy and exergy efficiencies are considered by many to be useful for the assessment of energy conversion and other systems and for efficiency improvement. By considering both of these efficiencies, the quality and quantity of the energy used to achieve a given objective is considered and the degree to which efficient and effective use of energy resources is achieved can be understood. Improving efficiencies of energy systems is an important challenge for meeting energy policy objectives. Reductions in energy use can assist in attaining energy security objectives. Also, efficient energy utilization and the introduction of renewable energy technologies can significantly help solve environmental issues. Increased energy efficiency benefits the environment by avoiding energy use and the corresponding resource consumption and pollution generation. From an economic as well as an environmental perspective, improved energy efficiency has great potential [2].

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2.6.1 What Is Exergy?

The useful work potential of a given amount of energy at a specified state is called *exergy*. It is also called the availability or available energy. The work potential of the energy contained in a system at a specified state, relative to a reference (dead) state, is simply the maximum useful work that can be obtained from the system [12].

A system is said to be in the dead-state when it is in thermodynamic equilibrium with its environment. At the dead-state, a system is at the temperature and pressure of its environment (in thermal and mechanical equilibrium), it has no kinetic or potential energy relative to the environment (zero velocity and zero elevation above a reference level), and it does not react with the environment (chemically inert). Also, there are no unbalanced magnetic, electrical, and surface tension effects

between the system and its surroundings, if these are relevant to the situation at hand. The properties of a system at the dead-state are denoted by the subscript zero, for example, P_0 , T_0 , h_0 , u_0 , and s_0 . Unless specified otherwise, the dead-state temperature and pressure are taken to be $T_0 = 25^\circ\text{C}$ (77°F) and $P_0 = 1$ atm (101.325 kPa or 14.7 psia). A system has zero exergy at the dead-state.

The notion that a system must go to the dead-state at the end of the process to maximize work output can be explained as follows. If the system temperature at the final state is greater (or less) than the temperature of the environment it is in, we can always produce additional work by running a heat engine between these two temperature levels. If the final pressure is greater (or less) than the pressure of the environment, we can still obtain work by letting the system expand to the pressure of the environment. If the final velocity of the system is not zero, we can catch that extra kinetic energy by a turbine and convert it to rotating shaft work, and so on. No work can be produced from a system that is initially at the dead-state. The atmosphere around us contains a tremendous amount of energy. However, the atmosphere is in the dead-state, and the energy it contains has no work potential.

Therefore, we conclude that a system delivers the maximum possible work as it undergoes a reversible process from the specified initial state to the state of its environment, that is, the dead-state. It is important to realize that exergy does not represent the amount of work that a work-producing device will actually deliver upon installation. Rather, it represents the upper limit on the amount of work a device can deliver without violating any thermodynamic laws. There will always be a difference, large or small, between exergy and the actual work delivered by a device. This difference represents the available room that engineers have for improvement especially for greener buildings and more sustainable buildings per ASHRAE's Sustainability Roadmap.

Note that the exergy of a system at a specified state depends on the conditions of the environment (the dead-state) as well as the properties of the system. Therefore, exergy is a property of the system–environment combination and not of the system alone. Altering the environment is another way of increasing exergy, but it is definitely not an easy alternative.

The work potential or exergy of the kinetic energy of a system is equal to the kinetic energy itself because it can be entirely converted to work. Similarly, exergy of potential energy is equal to the potential energy itself. On the other hand, the internal energy and enthalpy of a system are not entirely available for work, and only part of the thermal energy of a system can be converted to work. In other words, the exergy of thermal energy is less than the magnitude of thermal energy.

2.6.2 *Reversibility and Irreversibility*

These two concepts are highly important in the analysis of thermodynamic processes and systems. The *reversibility* refers to a process during which both the system and its surroundings can be returned to their initial states. The irreversibility is associated

with the destruction of exergy, and during an irreversible process, both the system and its surroundings cannot be returned to their initial states because of the irreversibilities occurring, for example, friction, heat rejection, electrical and mechanical effects, and the like.

2.6.3 Reversible Work and Exergy Destruction

The *reversible work* W_{rev} is defined as the maximum amount of useful work output or the minimum work input for a system undergoing a process between the specified initial and final states in a totally reversible manner.

Any difference between the reversible work W_{rev} and the actual work W_u is due to the irreversibilities present during the process, and this difference is called irreversibility or exergy destroyed. It is expressed as

$$X_{\text{destroyed}} = W_{\text{rev,out}} - W_{\text{out}} \quad \text{or} \quad X_{\text{destroyed}} = W_{\text{in}} - W_{\text{rev,in}} \quad (2.32)$$

Irreversibility is a positive quantity for all actual (irreversible) processes because $W_{\text{rev}} \geq W$ for work-producing devices and $W_{\text{rev}} \leq W$ for work-consuming devices.

Irreversibility can be viewed as the wasted work potential or the lost opportunity to do useful work. It represents the energy that could have been converted to work but was not. It is important to note that lost opportunities manifest themselves in environmental degradation and avoidable emissions. The smaller the irreversibility associated with a process, the greater the work that is produced (or the smaller the work that is consumed). The performance of a system can be improved by minimizing the irreversibility associated with it.

2.6.4 Exergy Change

A closed system, in general, may possess kinetic and potential energies, and in the absence of electric, magnetic, and surface tension effects, the total energy of a closed system is equal to the sum of its internal, kinetic, and potential energies. Noting that kinetic and potential energies themselves are forms of exergy, the exergy of a closed system of mass m is given by

$$X = (U - U_0) + P_0(V - V_0) - T_0(S - S_0) + m\frac{V^2}{2} + mgz \quad (2.33)$$

where the properties with the subscript zero represent those at the dead-state. On a unit mass basis, the closed system (or nonflow) exergy is expressed as

$$\phi = (u - u_0) + P_0(v - v_0) - T_0(s - s_0) + \frac{V^2}{2} + gz \quad (2.34)$$

The exergy change of a closed system during a process is simply the difference between the final and initial exergies of the system as follows:

$$\Delta X = U_2 - U_1 + P_0(V_2 - V_1) - T_0(S_2 - S_1) + m \frac{V_2^2 - V_1^2}{2} + mg(z_2 - z_1) \quad (2.35)$$

For stationary closed systems, the kinetic and potential energy terms drop out. The exergy of a flowing fluid is also called *flow* (or *stream*) *exergy*, and is given by

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{V^2}{2} + gz \quad (2.36)$$

Then the *exergy change* of a fluid stream as it undergoes a process from state 1 to state 2 becomes

$$\Delta\psi = \psi_2 - \psi_1 = (h_2 - h_1) - T_0(s_2 - s_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1) \quad (2.37)$$

For fluid streams with negligible kinetic and potential energies, the kinetic and potential energy terms drop out.

Note that the exergy change of a closed system or a fluid stream represents the maximum amount of useful work that can be done (or the minimum amount of useful work that needs to be supplied if it is negative) as the system changes from state 1 to state 2 in a specified environment, and represents the reversible work W_{rev} . It is independent of the type of process executed, the kind of system used, and the nature of energy interactions with the surroundings. Also note that the exergy of a closed system cannot be negative, but the exergy of a flow stream can at pressures below the environment pressure P_0 .

2.6.5 Exergy Transfer Mechanisms

Heat transfer Q at a location at thermodynamic temperature T is always accompanied by exergy transfer X_{heat} in the amount of

$$X_{\text{heat}} = \left(1 - \frac{T_0}{T}\right)Q \quad (2.38)$$

Exergy is the useful work potential, and the exergy transfer by work can simply be expressed as

$$X_{\text{work}} = W \quad (2.39)$$

and for boundary work,

$$X_{\text{work}} = W - W_{\text{surr}} = P_0(V_2 - V_1) \quad (2.40)$$

where P_0 is the atmospheric pressure and V_1 and V_2 are the initial and final volumes of the system.

Exergy transfer by mass is

$$X_{\text{mass}} = m\psi = m \left[(h - h_0) - T_0(s - s_0) + \frac{V^2}{2} + gz \right] \quad (2.41)$$

2.6.6 Exergy Balance

The nature of exergy is opposite to that of entropy in that exergy can be destroyed, but it cannot be created. Therefore, the exergy change of a system during a process is less than the exergy transfer by an amount equal to the exergy destroyed during the process within the system boundaries. Then the decrease of exergy principle can be expressed as

$$X_{\text{in}} - X_{\text{out}} - X_{\text{destroyed}} = \Delta X_{\text{system}} \quad (2.42)$$

In rate form,

$$\dot{X}_{\text{in}} - \dot{X}_{\text{out}} - \dot{X}_{\text{destroyed}} = \left(\frac{dX}{dt} \right)_{\text{CV}} \quad (2.43)$$

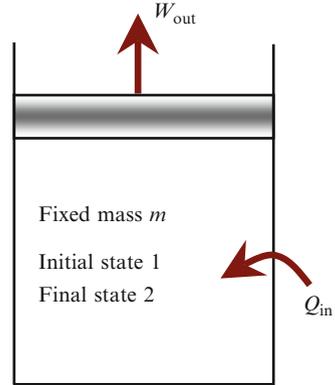
This relation is referred to as the exergy balance and can be stated as the exergy change of a system during a process is equal to the difference between the net exergy transfer through the system boundary and the exergy destroyed within the system boundaries as a result of irreversibilities. Exergy can be transferred to or from a system by heat, work, and mass.

Irreversibilities such as friction, mixing, chemical reactions, heat transfer through a finite temperature difference, unrestrained expansion, and nonquasi-equilibrium compression or expansion always generate entropy, and anything that generates entropy always destroys exergy. The exergy destroyed is proportional to the entropy generated, and is expressed as

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \quad (2.44)$$

Exergy destruction during a process can be determined from an exergy balance on the system or from the entropy generation using (2.44).

Fig. 2.4 A closed system involving heat input Q_{in} and boundary work output W_{out}



A closed system, in general, may possess kinetic and potential energies as the total energy involved. The exergy change of a closed system during a process is simply the exergy difference between the final state 2 and initial state 1 of the system. For a stationary closed system involving heat input Q_{in} and boundary work output W_{out} as shown in Fig. 2.4, mass, energy, entropy, and exergy balances can be expressed as

$$\text{Mass balance :} \quad m_1 = m_2 = \text{constant} \quad (2.45)$$

$$\text{Energy balance :} \quad Q_{in} - W_{out} = m(u_2 - u_1) \quad (2.46)$$

$$\text{Entropy balance :} \quad \frac{Q_{in}}{T_s} + S_{gen} = m(s_2 - s_1) \quad (2.47)$$

Exergy balance :

$$Q_{in} \left(1 - \frac{T_0}{T_s} \right) - [W_{out} - P_0(V_2 - V_1)] - X_{destroyed} = X_2 - X_1 \quad (2.48)$$

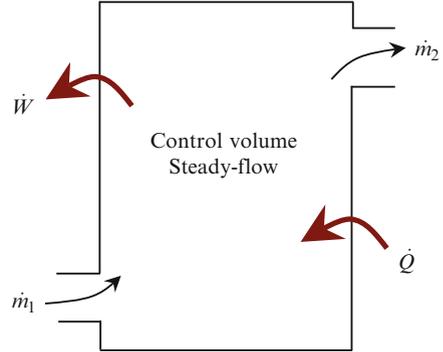
where u is internal energy, s is entropy, T_s is source temperature, T_0 is the dead-state (environment) temperature, S_{gen} is entropy generation, P_0 is the dead-state pressure, and V is volume. The exergy of a closed system is either positive or zero, and never becomes negative.

For a control volume involving a steady-flow process with heat input and power output as shown in Fig. 2.5, mass, energy, entropy, and exergy balances can be expressed as

$$\text{Mass balance :} \quad \dot{m}_1 = \dot{m}_2 \quad (2.49)$$

$$\text{Energy balance :} \quad \dot{m}_1 h_1 + \dot{Q}_{in} = \dot{m}_2 h_2 + \dot{W}_{out} \quad (2.50)$$

Fig. 2.5 A control volume involving heat input and power output



$$\text{Entropy balance : } \frac{\dot{Q}_{\text{in}}}{T_s} + \dot{m}_1 s_1 + \dot{S}_{\text{gen}} = \dot{m}_2 s_2 \quad (2.51)$$

$$\text{Exergy balance : } \dot{Q}_{\text{in}} \left(1 - \frac{T_0}{T_s} \right) + \dot{m}_1 \psi_1 = \dot{m}_2 \psi_2 + \dot{W}_{\text{out}} + \dot{X}_{\text{destroyed}} \quad (2.52)$$

where specific exergy of a flowing fluid (i.e., flow exergy) is given by

$$\psi = h - h_0 - T_0(s - s_0) \quad (2.53)$$

In these equations, kinetic and potential energy changes are assumed to be negligible. Most control volumes encountered in practice such as turbines, compressors, heat exchangers, pipes, and ducts operate steadily, and thus they experience no changes in their mass, energy, entropy, and exergy contents as well as their volumes. The rate of exergy entering a steady-flow system in all forms (heat, work, mass transfer) must be equal to the amount of exergy leaving plus the exergy destroyed.



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