Chapter 13

INTRODUCTION TO THE SECOND LAW

> There is good reason for *wanting* to violate the Second Law, for if it could be done, all of man's energy requirements could forever be met without any depletion of resources or pollution of his surroundings.
>
> – H.C. Van Ness (*Understanding Thermodynamics*)

Learning thermodynamics even at an introductory level cannot be considered complete without being told what the second law is all about. This chapter introduces the second law to a beginner in an unconventional way. The objective of this chapter is to make the students know why it is important to learn the second law, and what role it has in the thermodynamic analyses of engineering systems.

13.1 The Second Law

In this book, we adopt the most general approach to present the Second Law of Thermodynamics, which is that of Clausius. He made the following statement of the second law in 1865:

> **Total entropy change of any system and its surroundings is positive for a real process, and it approaches zero when the real process approaches a reversible process.**

The mathematical equivalence of the above statement of the second law is as follows:

$$\Delta S_{total} \begin{cases} > & 0 \text{ for a real (irreversible) process} \\ = & 0 \text{ for a reversible process} \\ < & 0 \text{ for an impossible process} \end{cases} \qquad (13.1)$$

The second law is a fundamental law, which means nobody has either proved or disproved the second law yet. It contains in it information that has been gathered over several hundred years of observations and experimentations with what is possible and what is not possible in reality.

`Student:` Teacher, the first law states energy is conserved. It is easy to understand what the first law is all about, and therefore to accept it as true. But, the second law does not make any sense.

`Teacher:` Well, let me put it this way. The second law of thermodynamics states that the total entropy of a system and its surroundings together is conserved for a reversible process, and it increases for a real, I mean physically realizable, process.

`Student:` Why should the total entropy of a system and its surroundings together increases for a real process? What is that physical entity that we measure using this entropy?

`Teacher:` It is a bit difficult to answer that question since it is impossible to relate entropy to a single physical entity. Let me only tell you that entropy is a property that provides a measure of the molecular disorder.

`Student:` What is the connection between molecular disorder and the second law?

`Teacher:` The Nature, it appears, prefers the direction of increasing molecular disorder. Entropy could be used to measure the degree of molecular disorder. Thus, we could say that for any thermodynamic process to occur in real life, the total entropy change of the system and its surroundings, which is the measure of the total molecular disorder of the system and its surroundings, must increase.

`Student:` Oh... I see.

13.2 Evaluation of Total Entropy Change

Since the value of ΔS can be used to determine whether a process is real, reversible or impossible, we need to learn about how to determine ΔS. We shall do that in this section.

For a closed system,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \tag{13.2}$$

where the label 'sys' stands for system and the label '$surr$' stands for surroundings.

Since S is a property, ΔS_{sys} can be evaluated using the following:

$$\Delta S_{sys} = m_{sys}\,\Delta s_{sys} = m_{sys}\,(s_f - s_o)_{sys} \tag{13.3}$$

where the subscript f stands for the final state and the subscript o stands for the initial state.

If the surroundings has a finite mass then the entropy difference between the final and the initial states of this finite mass would give the entropy change of the surroundings. We could therefore use

$$\Delta S_{surr} = m_{surr}\,\Delta s_{surr} = m_{surr}\,(s_f - s_o)_{surr} \tag{13.4}$$

Expressions developed in Chapter 11 for Δs of various substances could be used to evaluate Δs_{sys} and Δs_{surr} of (13.3) and (13.4), as will be demonstrated in the worked examples of this chapter.

The surroundings is, however, often taken as a **thermal reservoir** of infinite heat capacity. A thermal reservoir is assumed to remain at a constant temperature regardless of the heat transferred to or from the reservoir. It is also assumed that no irreversibilities occur within the reservoir. With these assumptions, the entropy change of the surroundings taken as a thermal reservoir is written as

$$\Delta S_{surr} = \frac{(Q_{in})_{surr}}{T_{surr}} \tag{13.5}$$

where $(Q_{in})_{surr}$ denotes the finite amount of heat transferred to the surroundings from the system during the process, and T_{surr} denotes the constant temperature of the surroundings in the Kelvin scale.

If the system is thermally isolated from the surroundings during the process, that is, in an adiabatic process, there is no heat exchange between the system and the surroundings. Therefore,

$$\Delta S_{surr} = 0$$

which simplifies (13.2) to the following:

$$\Delta S_{total} = \Delta S_{sys} \quad \text{for an adiabatic process.} \tag{13.6}$$

Using (13.3), we could write (13.6) as

$$\Delta S_{total} = m_{sys}\,(s_f - s_o)_{sys} \quad \text{for an adiabatic process.} \tag{13.7}$$

If the given adiabatic process takes place reversibly then, of course, we know that the entropy of the system remains a constant (see Section 11.4). Therefore, (13.7) reduces to

$$\Delta S_{total} = 0 \quad \text{for a reversible adiabatic process.} \tag{13.8}$$

To evaluate the entropy change for an open system, we need to incorporate the entropy of the matter that enters and leaves the system. Since we will mostly be working with steady flow processes, let us get the expression for the steady flow processes, which is the following:

$$\frac{d(\Delta S_{total})}{dt} = \sum \dot{m}_e\, s_e - \sum \dot{m}_i\, s_i + \frac{d(\Delta S_{surr})}{dt} \tag{13.9}$$

where the subscript e stands for the exit and the subscript i stands for the inlet.

If the surroundings is taken as a thermal reservoir at a constant temperature of T_{surr} K, we get

$$\frac{d(\Delta S_{surr})}{dt} = \frac{(\dot{Q}_{in})_{surr}}{T_{surr}} \tag{13.10}$$

where $(\dot{Q}_{in})_{surr}$ denotes the rate at which heat is transferred from the system to the surroundings during the process.

For an adiabatic steady flow process, the system does not thermally interact with the surroundings. Therefore,

$$\frac{d(\Delta S_{total})}{dt} = \sum \dot{m}_e\, s_e - \sum \dot{m}_i\, s_i \tag{13.11}$$

13.3 Worked Examples

Example 13.1

A thermally insulated rigid box of negligible heat capacity is divided into equal halves by a partition of negligible mass. Initially, one compartment contains air at 2 bar and 400 K, and the other is evacuated. When the dividing partition is raptured, air will rush to fill the entire box. Show that this process is a irreversible process. It is a common assumption that air at low or moderate pressures behaves like an ideal gas.

Solution to Example 13.1

Let us evaluate the total entropy change of the system and its surroundings to determine if the given process is reversible or not. The system is isolated from the surroundings, and therefore

$$\Delta S_{total} = \Delta S_{sys} = m_{air}\, \Delta s_{air}$$

Since air is assumed to behave as an ideal gas and since air volume has doubled during the process, we could use (11.23) or (11.25) to determine Δs_{air} as follows:

$$\Delta s_{air} = C_v \ln\left(T_f/T_o\right) + R \ln\left(2\right) = C_v \ln\left(P_f/P_o\right) + C_p \ln\left(2\right)$$

Let us now determine the temperature or pressure ratio between the final and the initial equilibrium states of the process. Since the entire system is isolated from its surroundings, the internal energy of the system remains constant throughout the process. Since air is assumed to behave as an ideal gas, and since the internal energy of an ideal gas is a function of temperature alone, the temperature at the final equilibrium state is also 400 K. Thus, $\ln(T_f/T_o) = 0$. We therefore get

$$\Delta S_{total} = m_{air}\,\Delta s_{air} = m_{air}\,R\,\ln(2) > 0$$

Thus, according to the second law given by (13.1), the given process is a irreversible process. We, of course, know that the expansion of air into vacuum is unrestrained, and therefore the expansion process is far from reversible. The second law has just proven it.

Example 13.2

Hot gases leaving the turbine of a turbojet engine is reported to enter the nozzle of the turbojet engine at 6 bar and 975 K and exit the nozzle at 0.9 bar and 925 m/s. Determine if such a flow is possible in reality. Ignore the speed of the gases at the nozzle entrance. Assume that the gases behave as ideal gas and that $C_p = 1.005$ kJ/kg · K and $\gamma = 1.4$. Also, assume steady adiabatic flow through the nozzle.

Solution to Example 13.2

Using the steady flow energy equation applied to the steady adiabatic flow of an ideal gas through the nozzle, we get T_e, the temperature at the nozzle exit, as

$$T_e = T_i - \frac{c_e^2 - c_i^2}{2\,C_p} = 975\text{ K} - \frac{925^2}{2\times 1005}\text{ K} = 549.3\text{ K}$$

Since the flow through the adiabatic nozzle exchanges no heat with its surroundings, using (13.11) and (11.24), we get

$$\begin{aligned}
\frac{d(\Delta S_{total})}{dt} &= \dot{m}\,(s_e - s_i) = \dot{m}\left[C_p \ln\left(\frac{T_e}{T_i}\right) - R\ln\left(\frac{P_e}{P_i}\right)\right] \\
&= \dot{m}\,R\left[\frac{1.4}{1.4-1}\ln\left(\frac{549.3}{975}\right) - \ln\left(\frac{0.9}{6}\right)\right] \\
&= -0.11\,\dot{m}\,R < 0
\end{aligned}$$

Thus, according to the second law given by (13.1), the given process is an impossible process.

Example 13.3

Determine the maximum possible speed realizable at the nozzle exit of **Example 13.2** for the given inlet condition and exit pressure.

Solution to Example 13.3

At the reversible limit, $d(\Delta S_{total})/dt) = 0$ for the flow through the adiabatic nozzle. Therefore, we get the temperature at the nozzle exit, T_e, as

$$\dot{m}\,R\left[\frac{1.4}{1.4-1}\ln\left(\frac{T_e}{975}\right)-\ln\left(\frac{0.9}{6}\right)\right]=0$$

which gives $T_e = 567$ K.

Using this exit temperature in the steady flow energy equation applicable for the flow through adiabatic nozzle, we get the speed at the nozzle exit, c_e, as

$$c_e=\sqrt{2\times C_p(T_i-T_e)}=\sqrt{2\times 1005\times(975-567)}=905.5\text{ m/s}$$

which is the maximum possible speed realizable at the nozzle exit for the given conditions.

Example 13.4

A steady flow of steam enters an adiabatic turbine at 60 bar and 400°C with negligible velocity. It is reported to leave the nozzle at 3 bar as saturated steam. Is that possible?

Solution to Example 13.4

The specific entropy of steam at the entrance of the turbine can be found from a Steam Table as $s_e = s$ at 60 bar and 400°C = 6.541 kJ/kg·K. The specific entropy of steam at the exit of the turbine is found from a Steam Table as $s_i = s$ of saturated steam at 3 bar = 6.993 kJ/kg·K.

Therefore, for steady flow through an adiabatic turbine,

$$\frac{d(\Delta S_{total})}{dt} = \dot{m}\,(s_e - s_i) = \dot{m}\,(6.541 - 6.993) < 0$$

Thus, according to the second law given by (13.1), the given process is not possible in reality.

Example 13.5

Calculate the entropy change for the process where 3 kg of liquid water at 30°C is cooled until it freezes at 0°C. Take C_{water} as 4.2 kJ/kg·K, and the latent heat of freezing at 0°C as −333 kJ/kg.

Solution to Example 13.5

Considering water as an incompressible substance, we could use (11.22) to determine the entropy change for the process, in which the temperature of water is reduced from 30°C to 0°C, as follows:

$$\Delta s = (4.2 \text{ kJ/kg}\cdot\text{K}) \times \ln(273/303) = -0.44 \text{ kJ/kg}\cdot\text{K}$$

Conversion of water to ice occurs at a constant temperature of 0°C, during which v changes but P remains constant. Thus, let us start with $T\,ds = dh - v\,dP$, which reduces to $T\,ds = dh$ for a constant-pressure process such as the one considered here. Therefore, we get

$$\Delta s = \int \frac{dh}{T} = \frac{\Delta h}{T}$$

for the given constant-pressure and constant-temperature phase change process.

Since Δh for the process of water turning into ice at 0°C is the latent heat of freezing, we get

$$\Delta s = \frac{-333 \text{ kJ/kg}}{273 \text{ K}} = -1.22 \text{ kJ/kg}\cdot\text{K}$$

The total change in the entropy for the given process is therefore

$$\Delta S_{sys} = 3 \text{ kg} \times (-0.44 - 1.22) \text{ kJ/kg}\cdot\text{K} = -4.98 \text{ kJ/K} \tag{13.12}$$

`Student:` Teacher, the total entropy change of the system is negative in the above example. According the second law, it is then an impossible process. How could that be? We know that water can be frozen to get ice. What is wrong?

`Teacher:` Nothing is wrong, dear Student. Observe that it is the total entropy change of the *system* that takes a negative value, not the total entropy change of the system and the surroundings. The given system has interacted with its surroundings during cooling, by losing heat to the surroundings. Therefore, we need to evaluate the entropy change of the surroundings, and add that value to the entropy change of the system to get the total entropy change of the system and its surroundings. It is this total that should take a positive value for the process to be a real process.

Example 13.6

Calculate the total entropy change of the system and its surroundings for the process given in **Example 13.5**. Take the surroundings to be a thermal reservoir at −20°C.

Solution to Example 13.6

The entropy change of the system is calculated in the **Solution to Example 13.5**, and is given by (13.12). Now, let us evaluate the entropy change of the surroundings. Since the surroundings is assumed to be a thermal reservoir at −20°C, we could use (13.5) to get ΔS_{surr} as follows:

$$\Delta S_{surr} = \frac{(Q_{in})_{surr}}{253 \text{ K}} \tag{13.13}$$

where $(Q_{in})_{surr}$ is the heat lost by the system to the surroundings.

The heat lost by water when it is cooled from 30°C to 0°C is evaluated using (3 kg) × (4.2 kJ/kg·K) × (303 − 273) K, which becomes 378 kJ. Heat lost during the conversion of water at 0°C to ice at 0°C is evaluated using (3 kg) × 333 kJ/kg, which becomes 999 kJ.

The total heat lost to the surroundings is therefore 1377 kJ. Substituting it in (13.13), we get

$$\Delta S_{surr} = \frac{1377 \text{ kJ}}{253 \text{ K}} = 5.44 \text{ kJ/K} \tag{13.14}$$

Combining (13.12) and (13.14), we get

$$\Delta S_{total} = 0.46 \text{ kJ/K} > 0$$

Therefore, according to the second law, the process considered is a real (irreversible) process.

`Student:` Teacher, you have assumed that the surroundings was at −20°C in working out the above example. What if I take the surroundings to be at the room temperature, say, 30°C. Will I still get $\Delta S_{total} > 0$?

`Teacher:` You can't do that. How could the system, which is cooled from 30°C to 0°C, lose heat to a surroundings that is at a higher temperature than the system?

`Student:` Yes, that is true.... But, Teacher, it happens with the refrigerator. Doesn't it?

`Teacher:` Yes, it does. Heat is transferred from the inside of the refrigerator, which is at a much lower temperature than the atmospheric temperature, to the surroundings, which is at atmospheric temperature. That is correct.

`Student:` How does that happen, Teacher?

`Teacher:` A refrigerator cannot lose heat to its surroundings unless we provide work in the form of electricity to operate its compressor. Do you agree with that?

`Student:` Yes, I do. I know about the compressor in the refrigerator. If the compressor fails then refrigerator does not function. Well, how does a refrigerator work?

`Teacher:` Each refrigerator has an engine, which consists of a fluid known as refrigerant. Are you familiar with that?

`Student:` I know about the refrigerant used in a refrigerator. I know that CFCs, the chemicals that make a hole in the ozone layer, are used as refrigerants. But, nowadays, it is being replaced by other chemicals that does not damage the ozone layer.

`Teacher:` It's very good that you know so much about refrigerants. Now, let me tell you about the cyclic process executed by the refrigerant in the refrigerator. The schematic diagram of a typical refrigeration cycle is given in Figure 13.1.

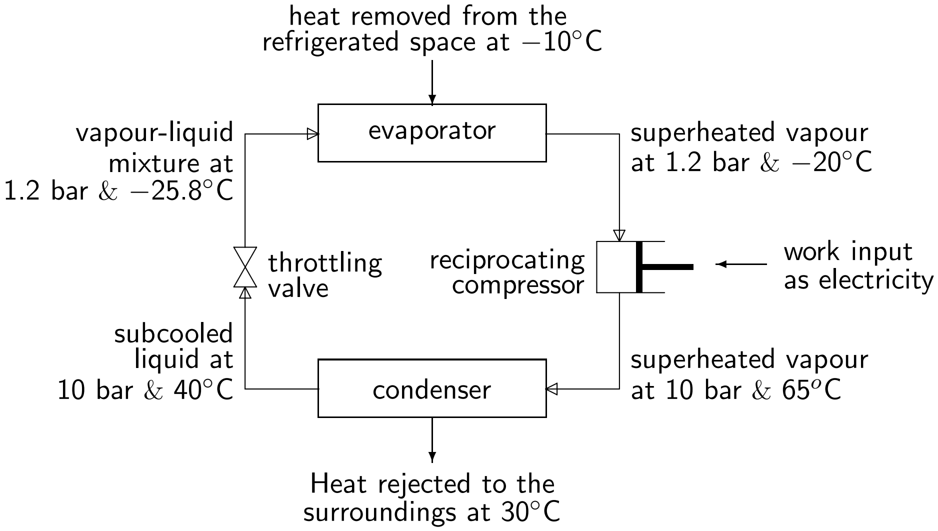

Figure 13.1 Schematic of a typical refrigeration cycle.

`Student:` Teacher, the figure looks complicated except for the compressor, throttling valve and the condenser. We have already learned about them in Chapter 10. Haven't we?

`Teacher:` Yes, you have. Let me explain the workings of the refrigeration cycle shown in the figure. First of all, let's take the freezer compartment of a refrigerator, which must be maintained, say, at −10°C. Heat must be continuously removed from the freezer space to maintain such a low temperature when the surrounding atmosphere is around 30°C. Do you agree with that?

`Student:` Yes, I do.

`Teacher:` Let us send a liquid, the refrigerant, at a temperature much lower than −10°C through the evaporator coil that is attached to the inner walls of the freezer compartment. Tell me what happens to the refrigerant then.

`Student:` Of course, heat will be transferred from the freezer space at −10°C to the refrigerant at a temperature much lower than −10°C.

`Teacher:` That's correct. The refrigerant entering the evaporator is usually maintained as a mixture of saturated liquid and vapour at a temperature at least 10 degrees below the freezer space temperature, and at a pressure slightly above the atmospheric pressure. The heat transferred from the freezer space to the refrigerant heats the refrigerant to a slightly superheated vapour state. This vapour is compressed to a pressure about 8 to 10 times the atmospheric pressure in a reciprocating type of compressor powered by electricity.

`Student:` Why are we compressing the refrigerant, Teacher?

`Teacher:` When the refrigerant vapour is compressed, its temperature would increase. We need to increase the temperature of the refrigerant well above the temperature of the surroundings, so that the refrigerant could lose all the heat that it has gained in the evaporator to the surroundings, as it passes through the condenser coil that is exposed to the atmosphere.

`Student:` I see, that is why the air around the refrigerator is warm. It explains why my cat loves to lie down on the refrigerator during the cold days.

`Teacher:` Yes, that is right.

`Student:` Okay, Teacher, I understand how the refrigeration cycle works. But, tell me why there is a throttling valve in the cycle.

`Teacher:` The temperature of the refrigerant leaving the condenser could not be reduced below the atmospheric temperature. Do you agree with that?

`Student:` Yes, I do. We could not lower the temperature of the refrigerant below the temperature of the atmosphere to which it is losing heat.

`Teacher:` That's correct. The refrigerant leaving the condenser at a temperature above the atmospheric temperature is throttled using a throttling valve to reduce the temperature of the refrigerant passing through it, to a value that is much below the atmospheric temperature.

`Student:` Well, I see why a throttling valve is needed.

`Teacher:` The refrigeration cycle is so designed that the temperature and the pressure reductions across the throttling valve, which is simply a capillary tube, will bring the refrigerant to the temperature and the pressure at which it enters the evaporator. In this way, the refrigeration cycle is completed and the same refrigerant is used over and over again.

`Student:` Oh, I see. That's neat. But... I have a question. It appears that the refrigerant is used and reused. Then, how it enters the atmosphere and destroys the ozone layer.

`Teacher:` Oh, well, the discarded refrigerators are the main culprits who let the refrigerant into the atmosphere. Now, I want you to take note of the fact that heat cannot be transferred from a lower temperature body to a higher temperature body unless work is provided to the engine, as with the refrigerators.

`Student:` Yes, I have noted that.

`Teacher:` In the following examples, we will prove that fact using the second law given by (13.1).

Example 13.7

Is it possible for an engine, whose working fluid operating in a cyclic process as in the refrigeration cycle discussed above, to transfer heat from a cooler reservoir to a hotter reservoir without producing any other effects on the surroundings?

Solution to Example 13.7

Let us consider the schematic of an engine shown in Figure 13.2, whose working fluid describe is said to describe a cyclic process. It receives Q_{in} amount of heat from the cold reservoir at T_L K and rejects Q_{out} amount of heat to the hot reservoir at T_H K, where $T_H > T_L$.

Since the system describes a cyclic process, the internal energy of the system remains a constant. Therefore, according to the first law, all heat removed from the cold reservoir could be transferred to the hot reservoir. That is,

$$Q_{in} = Q_{out} \tag{13.15}$$

Let us now calculate the total entropy change of the engine of Figure 13.2. The system undergoes a cyclic process and entropy is a property, and therefore the entropy of the system would not change. That is,

$$\Delta S_{sys} = 0 \tag{13.16}$$

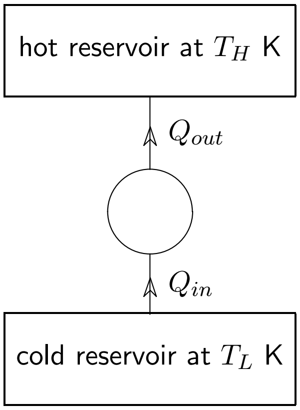

Figure 13.2 Heat transfer from a cooler reservoir to a hotter reservoir.

The surroundings consists of the hot reservoir at T_H K and the cold reservoir at T_L K. The entropy change of the surroundings can therefore be evaluated using (13.5) as follows:

$$\Delta S_{surr} = \frac{Q_{out}}{T_H} - \frac{Q_{in}}{T_L} \tag{13.17}$$

where the hot reservoir gains Q_{out} amount of heat from the system and the cold reservoir loses Q_{in} amount of heat to the system.

Combining (13.16) and (13.17), we get the total entropy change of the engine of Figure 13.2 as

$$\Delta S_{total} = \frac{Q_{out}}{T_H} - \frac{Q_{in}}{T_L} \tag{13.18}$$

Using (13.15), the above could be rewritten as

$$\Delta S_{total} = \left(\frac{T_L - T_H}{T_H\, T_L}\right) Q_{in} < 0$$

since T_L, the temperature of the cold reservoir, is less than T_H, the temperature of the hot reservoir.

According to the second law, given by (13.1), a process for which $\Delta S_{total} < 0$ is an impossible process. Thus, no engine, whose working fluid operating in a cyclic process, could transfer heat from a cooler reservoir to a hotter reservoir, without producing any other effects.

Example 13.8

Prove using the second law that it is possible for an engine, whose working fluid operating in a cyclic process, to remove heat from a cooler reservoir and rejects heat to a hotter reservoir, if work is supplied to the engine?

Solution to Example 13.8

The engine given in this example is what is known as the **refrigerator** or, as the **heat pump** in general, and the schematic of which is shown in Figure 13.3.

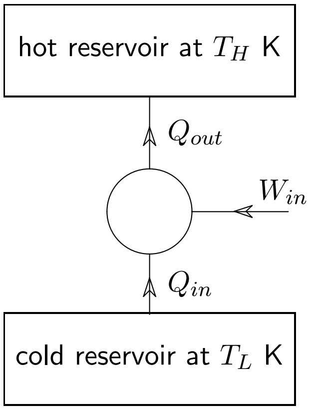

Figure 13.3 Schematic of a heat pump.

This example is similar to **Example 13.7**, except for the fact that the system is provided with work. Therefore, according to the first law,

$$Q_{in} + W_{in} = Q_{out} \tag{13.19}$$

The total entropy change of the heat pump of Figure 13.3 would be the same as that is given by (13.18). Eliminating Q_{out} from (13.18) using (13.19), we get

$$\begin{aligned} \Delta S_{total} &= \frac{Q_{in} + W_{in}}{T_H} - \frac{Q_{in}}{T_L} \\ &= \frac{W_{in}}{T_H} - \left(\frac{T_H - T_L}{T_H T_L}\right) Q_{in} \end{aligned} \tag{13.20}$$

For ΔS_{total} to be a positive quantity,

$$W_{in} > \left(\frac{T_H - T_L}{T_L}\right) Q_{in} \tag{13.21}$$

Thus, it is possible to construct an engine, whose working fluid operating in a cyclic process, capable of removing heat from a cooler reservoir and rejects heat to a hotter reservoir, if the work done on the working fluid of the engine satisfies (13.21).

Comment: From **Example 13.7** and **Example 13.8**, we shall conclude that it is impossible to construct an engine, whose working fluid operating in a cyclic process, capable of transferring heat from a cooler body to a hotter body, without producing no other effect. This is the famous **Clausius Statement of the Second Law**.

The ratio of heat removed from the cooler reservoir by the heat pump to the work supplied to the heat pump is known as the **coefficient of performance**, and is denoted by COP. From (13.21), we can determine the upper limit of the COP as follows:

$$COP = \frac{Q_{in}}{W_{in}} < \frac{T_L}{T_H - T_L} \tag{13.22}$$

Any heat pump that works at the upper limit of the COP will have $\Delta S_{total} = 0$, which means that such a heat pump operates as a reversible heat pump. A reversible heat pump is known as the **Carnot heat pump**, and its COP is known at the **Carnot** COP, given by

$$COP_{Carnot} = \frac{T_L}{T_H - T_L} \tag{13.23}$$

Example 13.9

Determine the minimum amount of work required to operate an air-conditioner which will maintain an indoor temperature of 25°C. The atmospheric temperature is at 36°C, and the heat generated indoor from the people and other heat generating devices are estimated to be 26 MJ/h. Determine also the heat rejected to the atmosphere by the air-conditioner.

Solution to Example 13.9

The air-conditioner functions as a heat pump removing 26 MJ/h of heat from the indoor space maintained at 25°C (which is the cooler reservoir) and rejecting heat to the atmosphere at 36°C (which is the hotter reservoir). Combining (13.22) and (13.23), we can write the coefficient of performance of an air-conditioner, as

$$COP = \frac{Q_{in}}{W_{in}} \leq COP_{Carnot}$$

which gives

$$W_{in} = \frac{Q_{in}}{COP} \geq \frac{Q_{in}}{COP_{Carnot}}$$

The minimum work required by the air-conditioner is therefore given by

$$(W_{in})_{min} = \frac{Q_{in}}{COP_{Carnot}}$$

We can calculate the COP using (13.23) as

$$COP_{Carnot} = \frac{T_L}{T_H - T_L} = \frac{273 + 25}{(273 + 36) - (273 + 25)} = 27.1$$

It is given that $Q_{in} = 26$ MJ/h, and therefore

$$(W_{in})_{min} = \frac{26 \text{ MJ/h}}{27.1} = 0.27 \text{ kW}$$

The minimum amount of heat rejected to the atmosphere by the air-conditioner is calculated as follows:

$$\begin{aligned} (Q_{out})_{min} &= Q_{in} + (W_{in})_{min} \\ &= 26 \text{ MJ/h} + \frac{26}{27.1} \text{ MJ/h} \approx 27 \text{ MJ/h} \end{aligned}$$

Comment: Note that making the living space cool and comfortable by air-conditioning results in additional amount of heat being rejected into the environment. At least 1 MJ/h of waste heat is added in the case considered in this example.

Example 13.10

Is it possible to convert all heat provided to an engine, whose working fluid operating in a cycling process, into useful work?

Solution to Example 13.10

Let us consider the engine shown in Figure 13.4. The working fluid of the engine, taken as the system, is said to operate a cyclic process. It receives Q_{in} amount of heat from the surroundings and does W_{out} amount of work on the surroundings.

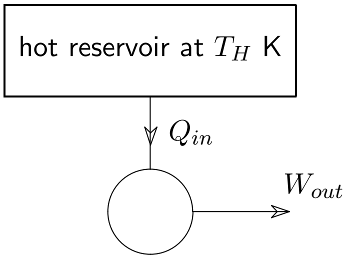

Figure 13.4 Schematic of an engine converting all heat into work.

Since the system describes a cyclic process, the internal energy of the system remains a constant. Therefore, according to the first law, all heat provided to the system is converted into work. That is, $W_{out} = Q_{in}$.

Well, what does the second law says about such a 100% conversion of heat into work? To answer this question, let us calculate the total entropy change of the engine of Figure 13.4. Following the methods used in the previous examples, we could write that $\Delta S_{sys} = 0$, and $\Delta S_{surr} = -(Q_{in}/T_H)$.

The total entropy change of the engine of Figure 13.4 is therefore

$$\Delta S_{total} = -\frac{Q_{in}}{T_H} < 0 \tag{13.24}$$

since Q_{in} and T_H are positive quantities.

According to the second law, given by (13.1), a process for which ΔS_{total} < 0 is an impossible process. Therefore, it is not possible to convert all heat provided to an engine, whose working fluid operating in a cycling process, into work.

Example 13.11

Prove using the second law that it is possible for an engine, whose working fluid operating in a cyclic process, to convert part of the heat that it receives from a hotter reservoir into work done on the surroundings, provided the remaining heat is rejected to a cooler reservoir.

Solution to Example 13.11

The engine given in this example is what is known as the **heat engine**, and the schematic of which is shown in Figure 13.5.

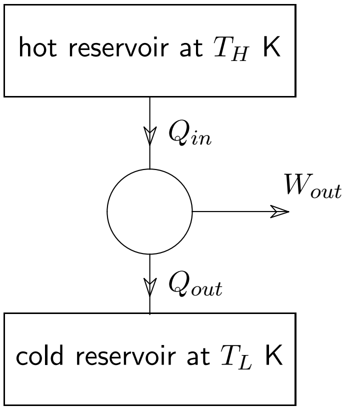

Figure 13.5 Schematic of a heat engine.

This example is similar to **Example 13.10**, except for the fact that the system rejects heat into a cooler reservoir. Therefore, according to the first law,

$$Q_{in} = W_{out} + Q_{out} \tag{13.25}$$

Let us calculate the total entropy change of the engine of Figure 13.5 following the methods used in the previous examples as follows: $\Delta S_{sys} = 0$, and $\Delta S_{surr} = -(Q_{in}/T_H) + (Q_{out}/T_L)$.

The total entropy change of the engine of Figure 13.5 is therefore

$$\Delta S_{total} = -\frac{Q_{in}}{T_H} + \frac{Q_{out}}{T_L} \tag{13.26}$$

Eliminating Q_{out} from (13.26) using (13.25), we get

$$\begin{aligned} \Delta S_{total} &= -\frac{Q_{in}}{T_H} + \frac{Q_{in} - W_{out}}{T_L} \\ &= \left(\frac{T_H - T_L}{T_H T_L}\right) Q_{in} - \frac{W_{out}}{T_L} \end{aligned} \tag{13.27}$$

For ΔS_{total} to be a positive quantity,

$$W_{out} < \left(\frac{T_H - T_L}{T_H}\right) Q_{in} \tag{13.28}$$

Thus, it is possible to construct an engine, whose working fluid operating in a cyclic process, to convert part of the heat it receives from a hotter reservoir into work done on the surroundings, and to reject the remaining heat to a cooler reservoir, provided (13.28) is satisfied.

Comment: From **Example 13.10** and **Example 13.11**, we shall conclude that it is impossible to construct an engine, whose working fluid operating in a cyclic process, capable of converting all heat it receives into useful work, without producing no other effect in its surroundings. This is the famous **Kelvin-Plank Statement of the Second Law**.

The ratio of work obtained from the heat engine to the heat provided to the heat engine is known as the **thermal efficiency**, and is denoted by η. From (13.28), we can determine the upper limit of the thermal efficiency as follows:

$$\eta = \frac{W_{out}}{Q_{in}} < 1 - \frac{T_L}{T_H} \tag{13.29}$$

Any heat engine that works at the upper limit of the thermal efficiency will have $\Delta S_{total} = 0$, which means that such a heat engine operates as a reversible heat engine. A reversible heat engine is known as the **Carnot heat engine**, and its thermal efficiency is known at the **Carnot efficiency**, denoted by

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H} \tag{13.30}$$

No heat engine can have a thermal efficiency higher than the Carnot efficiency, which is a function of the maximum and minimum temperatures across which the heat engine operates.

Increasing the temperature of the hotter reservoir and/or decreasing the temperature of the cooler reservoir are the only means by which the Carnot efficiency of a heat engine could be increased.

Example 13.12

Consider the steam turbine of **Example 12.4**, whose working fluid (water/steam) operates in a cyclic process. Take the hot gases providing heat to the steam generator as the hotter reservoir, and assume that it remains at a constant temperature of 500°C throughout the operation. Take the cooling water removing heat from the condenser as the cooler reservoir at a constant temperature of 27°C. If the heat input to the steam engine from the hotter reservoir is 155 MJ/s, determine the maximum work output possible from the heat engine, and the amount of heat rejected to the cooler reservoir.

Solution to Example 13.12

Combining (13.29) and (13.30), we can write that the thermal efficiency of a heat engine as

$$\eta = \frac{W_{out}}{Q_{in}} \leq \eta_{Carnot}$$

which gives

$$W_{out} = \eta \times Q_{in} \leq \eta_{Carnot} \times Q_{in}$$

The maximum work obtainable is therefore given by

$$(W_{out})_{max} = \eta_{Carnot} \times Q_{in}$$

We can calculate η_{Carnot} using (13.30) as

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H} = 1 - \frac{273 + 27}{273 + 500} = 61.2\%$$

It is given that $Q_{in} =$ 155 MJ/s, and therefore

$$(W_{out})_{max} = 0.612 \times 155 \text{ MJ/s} = 95 \text{ MW}$$

The minimum amount of heat rejected by the heat engine can be calculated using the first law as follows:

$$(Q_{out})_{min} = Q_{in} - (W_{out})_{max} = 155 \text{ MJ/s} - 95 \text{ MW} = 60 \text{ MJ/s}$$

Comment: For any real heat engine working between the reservoirs at 500°C and 27°C, the thermal efficiency would be less than 61.2%, which is the Carnot efficiency, the work output would be less than 95 MW, and the heat rejected by the engine would be more than 60 MJ/s.

Example 13.13

If the temperature of the cooler reservoir of the heat engine of **Example 13.12** is reduced to, say, −23°C, then the work output of the heat engine could be increased for the same 155 MJ/s of heat that the heat engine receives from the reservoir at 500°C. You therefore plan to use a cooler reservoir at −23°C for the heat engine. To maintain the temperature at −23°C, you plan to use a heat pump that operates between the −23°C reservoir and the original cooler reservoir of the heat engine of **Example 13.12** at 27°C. Assuming that all the heat rejected by the heat engine to the reservoir at −23°C is removed by the heat pump, determine the maximum net work output and the overall thermal efficiency of the combined system.

Solution to Example 13.13

Figure 13.6 shows the combined system. The heat pump could be operated only if we provide work to it, which is denoted as W_{in} is the figure. The net work output is therefore $W_{out} - W_{in}$, where W_{out} is the work output of the heat engine.

For the heat engine, following the procedure adopted in the **Solution to Example 13.12**, we get

$$\eta_{Carnot} = 1 - \frac{250}{773} = 0.677$$

and therefore the maximum work obtainable from the heat engine is given by

$$(W_{out})_{max} = \eta_{Carnot} \times Q_1 = 0.677 \times 155 \text{ MJ/s} = 105 \text{ MW}$$

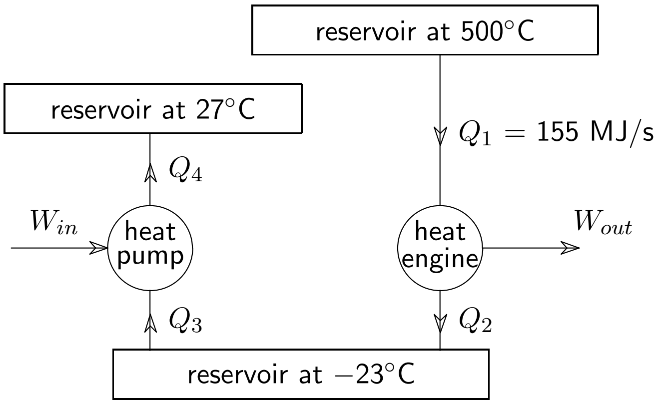

Figure 13.6 Schematic for Example 13.13.

Heat rejected by the heat engine to the reservoir at −23°C is

$$Q_2 = Q_1 - (W_{out})_{max} = 155 \text{ MJ/s} - 105 \text{ MW} = 50 \text{ MJ/s}$$

This amount of heat is removed by the heat pump from the reservoir at −23°C, and therefore

$$Q_3 = Q_2 = 50 \text{ MJ/s}$$

Combining (13.22) and (13.23), we can write the coefficient of performance of a heat pump as

$$COP = \frac{Q_3}{W_{in}} \leq COP_{Carnot}$$

which gives

$$W_{in} = \frac{Q_3}{COP} \geq \frac{Q_3}{COP_{Carnot}}$$

The minimum work required by the heat pump is therefore given by

$$(W_{in})_{min} = \frac{Q_3}{COP_{Carnot}}$$

We can calculate the COP using (13.23) as

$$COP_{Carnot} = \frac{T_L}{T_H - T_L} = \frac{250}{300 - 250} = 5$$

We know that $Q_3 = 50$ MJ/s, and therefore

$$(W_{in})_{min} = \frac{50 \text{ MJ/s}}{5} = 10 \text{ MW}$$

The net work output of the combined system is calculated as follows:

$$(W_{out})_{net} = (W_{out})_{max} - (W_{in})_{min} = 105 \text{ MW} - 10 \text{ MW} = 95 \text{ MW}$$

which is the maximum net work output obtainable from the combined system.

The overall thermal efficiency of the combined system is determined as follows:

$$\eta_{overall} = \frac{(W_{out})_{net}}{Q_1} = \frac{95 \text{ MW}}{155 \text{ MJ/s}} = 61.2$$

Comment: Observe that the maximum net work output and the overall thermal efficiency of the combined system are the same as the maximum work output and the thermal efficiency of the heat engine alone in **Example 13.12**. Therefore, it is of no advantage to use the combined system proposed in this example to generate the work required.

Example 13.14

A metal block A of 70 kg is at 800 K and a metal block B of 200 kg is at 300 K. A heat engine, the working fluid of which operating in a cyclic process, is to be operated using the two given metal blocks as the heat source and heat sink, respectively. It is reported that during a trial run, the temperature of the metal block A is reduced to 470 K and that of the metal block B is increased to 370 K. The specific heat of the metal is given as 0.45 kJ/kg · K. Verify the report by carrying out a second law analysis.

If the system satisfies the second law, determine the work output and the thermal efficiency of the heat engine.

Solution to Example 13.14

Consider the heat engine as the system and the metal blocks A and B as the surroundings. Since the heat engine describes a cyclic process, $\Delta S_{sys} = 0$. Therefore,

$$\Delta S_{total} = \Delta S_{surr} = \Delta S_A + \Delta S_B$$

Taking the metal blocks to be incompressible substances, we could use

(11.15) to calculate the entropy changes of blocks A and B as follows:

$$\begin{aligned}\Delta S_A &= (70\ \text{kg}) \times (0.45\ \text{kJ/kg}\cdot\text{K}) \times \ln\left(\frac{470}{800}\right) = -16.75\ \text{kJ/K} \\ \Delta S_B &= (200\ \text{kg}) \times (0.45\ \text{kJ/kg}\cdot\text{K}) \times \ln\left(\frac{370}{300}\right) = 18.88\ \text{kJ/K}\end{aligned}$$

Therefore,

$$\Delta S_{total} = -16.75\ \text{kJ/K} + 18.88\ \text{kJ/K} = 2.12\ \text{kJ/K} > 0$$

Since $\Delta S_{total} > 0$, according to the second law, the given system is physically realizable.

The work output of the engine, according to the first law, is given by the difference between the heat received by the engine from block A and the heat rejected by the engine to block B. Heat received by the engine from block A is given by 70 × 0.45 × (800 - 470) kJ = 10,395 kJ. Heat rejected by the engine to block B is given by 200 × 0.45 × (370 - 300) kJ = 6,300 kJ. The work output of the engine is therefore 4,095 kJ. And, the thermal efficiency of the engine is 39.4%.

Example 13.15

What should be the final temperature of block B of **Example 13.14** for the work output of the heat engine to reach its maximum? Assume all other data of **Example 13.14** remains unchanged. Determine also the value of the maximum work output and the corresponding thermal efficiency.

Solution to Example 13.15

The maximum work output could be obtained, in theory, when the system of **Example 13.14** reaches its reversible limit. That is, when $\Delta S_{total} = \Delta S_A + \Delta S_B = 0$, which gives

$$70 \times 0.45 \times \ln\left(\frac{470}{800}\right) + 200 \times 0.45 \times \ln\left(\frac{T_{Bf}}{300}\right) = 0$$

where T_{Bf} is the final temperature of block B.

Solving the above, we get T_{Bf} = 361.4 K. Therefore, heat rejected by the engine to block B will become 200 × 0.45 × (361.4 - 300) kJ = 5,526 kJ. Heat received by the engine from block A remains the same as in the **Solution to Example 13.14**, which is 10,395 kJ. The maximum work output will therefore be 4,869 kJ, and the corresponding thermal efficiency will be 46.8%.

Example 13.16

A reversible gas turbine, whose working fluid is considered to operate in a cyclic process, works between two thermal reservoirs, say A and B. The reservoir A is at 1200 K and the reservoir B is at 500 K. A reversible steam turbine is operated between the reservoir B and the atmosphere at 300 K. Determine the overall thermal efficiency of this idealized combined gas turbine - steam turbine plant.

Compare this overall thermal efficiency to the thermal efficiency of a reversible heat engine that would operate between the reservoirs at 1200 K and 300 K.

Solution to Example 13.16

The schematic of the combined power plant is shown in Figure 13.7. The overall thermal efficiency of the combined power plant would be

$$\eta_{overall} = \frac{(W_{out})_{gt} + (W_{out})_{st}}{Q_1}$$

From the data given for the reversible gas and steam turbines, we get

$$\begin{aligned} \eta_{gt} &= 1 - \frac{500}{1200} = 58.3\% \quad \text{and} \quad (W_{out})_{gt} = 0.583\,Q_1 \\ \eta_{st} &= 1 - \frac{300}{500} = 40.0\% \quad \text{and} \quad (W_{out})_{st} = 0.4\,Q_3 \end{aligned}$$

Assuming that all the heat rejected by the gas turbine to the reservoir at 500 K is taken by the steam turbine, we get

$$Q_3 = Q_2 = Q_1 - (W_{out})_{gt} = Q_1 - 0.583\,Q_1 = 0.417\,Q_1$$

which gives

$$(W_{out})_{st} = 0.4 \times 0.417\,Q_1 = 0.167\,Q_1$$

The overall thermal efficiency of the combined power plant therefore becomes

$$\eta_{overall} = \frac{0.583\,Q_1 + 0.167\,Q_1}{Q_1} = 75\%$$

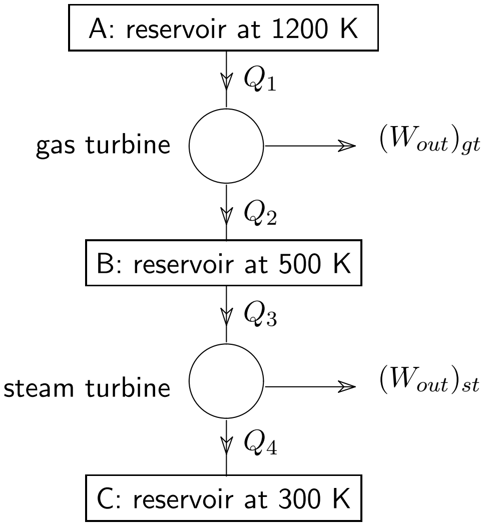

Figure 13.7 Schematic for Example 13.16.

For a reversible heat engine operating between the reservoirs at 1200 K and 300 K, the thermal efficiency is

$$\eta = 1 - \frac{300}{1200} = 75\%$$

The results show that regardless of whether we operate a single heat engine or a combined power plant, the thermal efficiency remains unchanged as far as the temperatures of the hotter reservoir and the cooler reservoir remain the same.

In reality, however, there are certain constraints in operating a gas turbine or a steam turbine alone between the two given temperature extremes to reach the kind of efficiencies that could be achieved by the combined power plant. The details of which is beyond the scope of this text book, and therefore will not be discussed here.

Example 13.17

The combined power plants are known for their improved thermal efficiency. The thermal efficiency of a newly installed combined power plant is about 48%. The plant operates between the maximum temperature of 1000 K and the atmospheric temperature of 300 K. A company that comes with foreign aid claims that they will be able to increase the thermal efficiency of the power plant to 70% by installing energy saving devices at a cost. You have been asked to advice the Minister of Energy on that. What will be your advice?

Solution to Example 13.17

A single (or even a combined) reversible heat engine operating between 1000 K and 300 K will have the following Carnot efficiency:

$$\eta_{Carnot} = 1 - \frac{300}{1000} = 70\%$$

No engine, however cleverly built, could have an efficiency that is higher than the Carnot efficiency, which is 70% in this case, as long as it is operated between the temperature extremes of 1000 K and 300 K.

Reaching the 70% thermal efficiency means that the combined power plant must be operated under reversible conditions. Even though, in theory, it is possible to improve the thermal efficiency to achieve the Carnot efficiency, it would be impossible to reach such efficiency in real life situations.

My advice to the Minister of Energy would be that the company's claim is not physically realizable.

13.4 Summary

- The mathematical equivalence of the second law is as follows:

$$\Delta S_{total} \begin{cases} > & 0 \text{ for a real (irreversible) process} \\ = & 0 \text{ for a reversible process} \\ < & 0 \text{ for an impossible process} \end{cases} \tag{13.1}$$

- For a closed system,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \tag{13.2}$$

  where

$$\Delta S_{sys} = m\,\Delta s_{sys} = m\,(s_f - s_o) \tag{13.3}$$

- If the surroundings has a finite mass,

$$\Delta S_{surr} = m_{surr}\,\Delta s_{surr} = m_{surr}\,(s_f - s_o)_{surr} \tag{13.4}$$

- A **thermal reservoir** is assumed to remain at a constant temperature regardless of the heat transferred to or from the reservoir. It is also assumed that no irreversibilities occur within the thermal reservoir.

- If the surroundings is taken as a thermal reservoir at a temperature of T_{surr} K then

$$\Delta S_{surr} = \frac{(Q_{in})_{surr}}{T_{surr}} \tag{13.5}$$

  where $(Q_{in})_{surr}$ denotes the finite amount of heat transferred to the surroundings from the system during the process.

- For an adiabatic process,

$$\Delta S_{total} = \Delta S_{sys} = m\,(s_f - s_o) \tag{13.7}$$

- For a reversible adiabatic process,

$$\Delta S_{total} = 0 \tag{13.8}$$

- For an open system,

$$\frac{d(\Delta S_{total})}{dt} = \sum \dot{m}_e\,s_e - \sum \dot{m}_i\,s_i + \frac{d(\Delta S_{surr})}{dt} \tag{13.9}$$

- If the surroundings of the open system is taken as a thermal reservoir at a constant temperature of T_{surr} K, then

$$\frac{d(\Delta S_{surr})}{dt} = \frac{(\dot{Q}_{in})_{surr}}{T_{surr}} \tag{13.10}$$

  where $(\dot{Q}_{in})_{surr}$ denotes the rate at which heat is transferred from the system to the surroundings during the process.

- For an adiabatic steady flow process,

$$\frac{d(\Delta S_{total})}{dt} = \sum \dot{m}_e \, s_e - \sum \dot{m}_i \, s_i \tag{13.11}$$

- A heat pump is a device, whose working fluid operating in a cyclic process, receives heat from a cooler reservoir and work from the surroundings, and rejects all that it received, as heat to a hotter reservoir.

- The coefficient of performance of a heat pump is given by

$$COP = \frac{Q_{in}}{W_{in}} < COP_{Carnot} \tag{13.22}$$

  where

$$COP_{Carnot} = \frac{T_L}{T_H - T_L} \tag{13.23}$$

- No heat pump can have a coefficient of performance higher than the Carnot coefficient of performance, which is a function of the maximum and minimum temperatures across which the heat pump operates.

- Heat engine is a device, whose working fluid operating in a cyclic process, receives heat from a hotter reservoir, does work on the surroundings, and rejects the remaining heat to a cooler reservoir.

- The thermal efficiency of a heat engine is given by

$$\eta = \frac{W_{out}}{Q_{in}} < \eta_{Carnot} \tag{13.29}$$

  where

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H} \tag{13.30}$$

- No heat engine can have a thermal efficiency higher than the Carnot efficiency, which is a function of the maximum and minimum temperatures across which the heat engine operates.