

Course Title:

Fundamental of Thermodynamics and Heat Transfer

Lecture 12 (Week 12):

Second Law of Thermodynamics

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Learning Objective of Lecture:

To impart a great deal of knowledge to undergraduate students on the following topics:

- ✓ Carnot Cycle and Heat Engine
- ✓ Heat Pump and Refrigerator
- ✓ Clausius Inequality
- ✓ Kelvin - Plank and Clausius Statements of the Second Law of Thermodynamics
- ✓ Equivalence of Kelvin – Plank and Clausius Statements

5.8. Carnot Cycle and Heat Engine

As mentioned earlier that a thermodynamic cycle consists of series of individual thermodynamic processes and the working substance returns to its initial state at the end of each cycle. Work is done by the working substance during one part of the cycle and it is done on the working substance during another part. The difference between these two is the net work delivered by the cycle. The efficiency of a cycle greatly depends on how the individual processes that make up the cycle are executed. The net work, thus the cycle efficiency, can be maximized by using processes that require the least amount of work and deliver the most, i.e. by using *reversible processes*. Therefore, it is no surprise that the most efficient cycles are reversible cycles, i.e. cycles that consist entirely of reversible processes. Reversible cycles cannot be achieved in practice because the irreversibilities associated with each process cannot be eliminated. However, reversible cycles provide upper limits on the performance of real cycles. Cyclic devices such as heat engines, heat pumps and refrigerators that work on reversible cycles serve as models to which actual heat engines, heat pumps and refrigerators can be compared. Reversible cycles along with Carnot cycle also serve as starting points in the development of actual cycles and are modified as needed to meet certain requirements.

5.8.1. Carnot Cycle

The best known reversible cycle is the *Carnot cycle*, first proposed in 1824 by French engineer Sadi Carnot. The theoretical heat engine that operates on the Carnot cycle is called the *Carnot heat engine*. The Carnot cycle is composed of four reversible processes e.g. two isothermal processes and two adiabatic processes. It can be executed either in a closed or a steady-flow (open) system. Let us consider a closed system that consists of a gas contained in an adiabatic piston - cylinder device, as shown in figure (5.13). The insulation of the cylinder head is such that it may be removed to bring the cylinder into contact with thermal reservoirs to provide heat transfer. Carnot cycle consists of the following four reversible processes in series as shown in Figure (5.13):

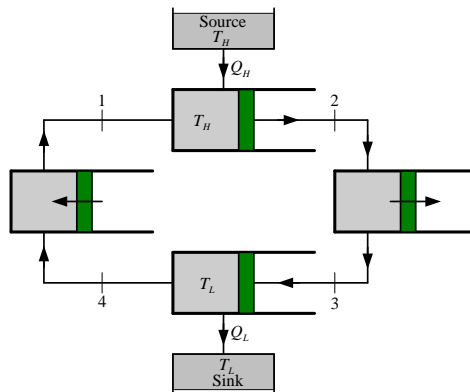


Figure 5.13. Execution of the Carnot cycle in a closed system [1]

Reversible Isothermal Heat Addition (Process 1 – 2)

Initially (state 1), the temperature of the working substance (gas) is T_H and the cylinder head is in close contact with a thermal reservoir or source at temperature T_H . Then heat is added or transferred to the gas inside the cylinder from the source and the gas is allowed to expand slowly thereby doing work on the surroundings. As the gas expands, the temperature of the gas tends to decrease. But as soon as the temperature drops by an infinitesimal amount dT , some heat is transferred from the source into the gas, raising the gas temperature to T_H . Thus, the gas temperature is kept constant at T_H . Since the temperature difference between the gas and the source never exceeds a differential amount dT , this is a reversible heat transfer process. It continues until the piston reaches state 2. Thus, during the process 1 - 2, the pressure of the gas decreases, its volume increases, its entropy increases and its temperature and enthalpy remain constant. The amount of total heat transferred to the gas during this process is Q_H .

Reversible Adiabatic (Isentropic) Expansion (Process 2 – 3)

At state 2, the thermal reservoir that was in contact with the cylinder head is removed and replaced by insulation so that the system becomes adiabatic. The gas continues to expand slowly, doing work on the surroundings until its temperature drops from T_H to T_L (state 3). The piston is assumed to be frictionless and the process to be quasi- equilibrium, so the process is reversible as well as adiabatic, i.e. isentropic. Thus, during process 2 – 3, the gas undergoes an isentropic expansion during which its pressure further decreases and its volume further increases. During the isentropic expansion process no heat is supplied to the system (gas) and hence it produces work due to expense of its internal energy. Therefore, during the isentropic expansion process, entropy of the system remains constant and its temperature and enthalpy decrease.

Reversible Isothermal Heat Rejection (Process 3 – 4)

At state 3, the insulation at the cylinder head is removed, and the cylinder is brought into contact with a thermal reservoir or a sink at temperature T_L . Then heat is rejected or transferred from the gas inside the cylinder to the sink and the gas is allowed to compressed slowly thereby doing work on the gas. As the gas is compressed, its temperature tends to rise. But as soon as it rises by an infinitesimal amount dT , heat is transferred from the gas to the sink, causing the gas temperature to drop to T_L . Thus, the gas temperature remains constant at T_L . Since the temperature difference between the gas and the sink never exceeds a differential amount dT , this is a reversible heat transfer or rejection process. It continues until the piston reaches state 4. Thus, during the process 3 - 4, pressure of the gas increases, its volume decreases, its entropy decreases, its temperature and enthalpy remain constant. The amount of heat rejected from the gas during this process is Q_L .

Reversible Adiabatic (Isentropic) Compression (Process 4 – 1)

At state 4, the low-temperature thermal reservoir is removed and the insulation is put back on the cylinder head. Now, the piston is pushed inward by an external force thereby doing work on the gas. The gas is further compressed under a reversible and adiabatic (isentropic) condition such that it returns to its initial state (state 1). During the process 4 – 1 its pressure further increases and its volume further decreases. During the isentropic compression process the work supplied to the system (gas) increases its internal energy because there is no heat loss from the gas. Therefore, during this process, entropy of the gas remains constant, its enthalpy increases and its temperature increases from T_L to T_H , which completes the cycle.

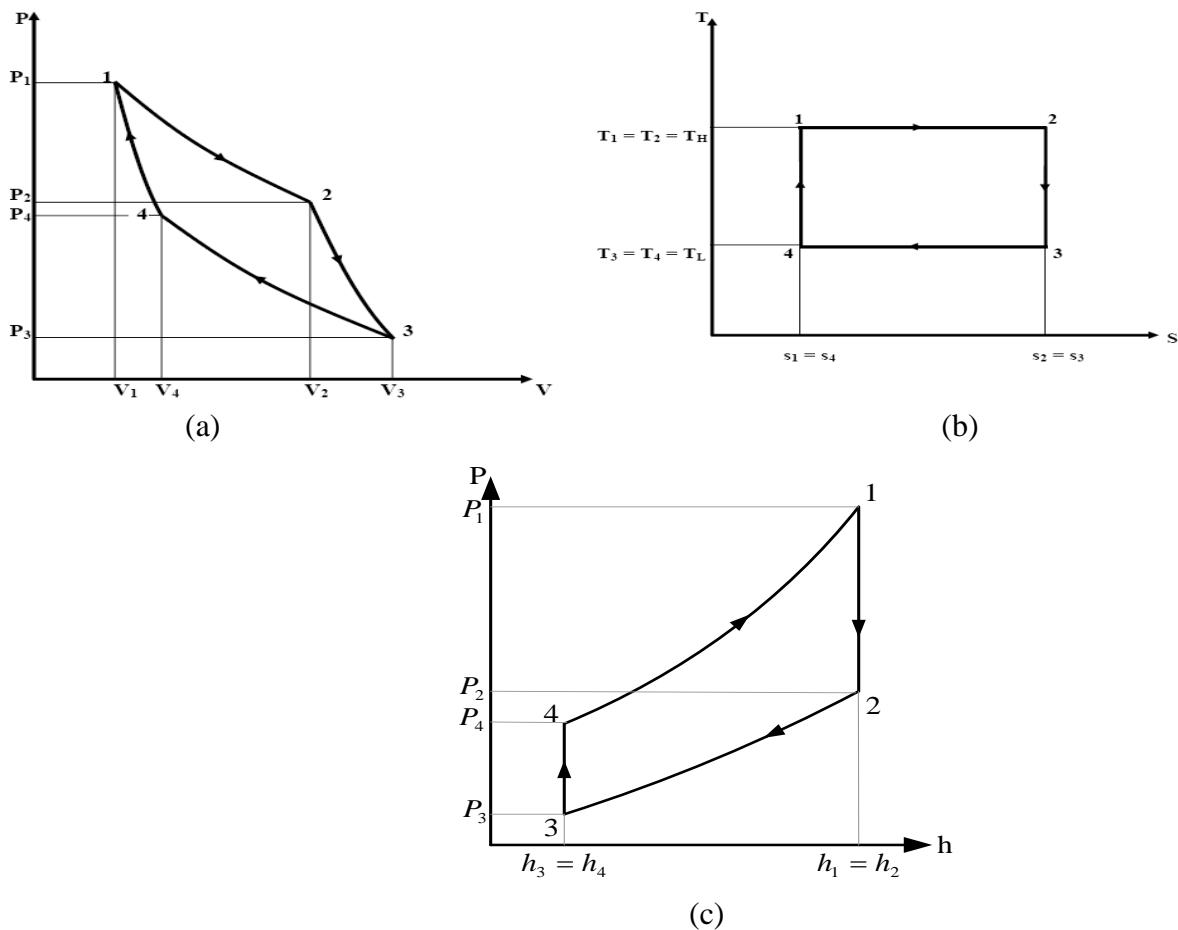


Figure 5.14. $P - V$, $T - S$ and $P - h$ diagrams for Carnot Cycle

The $P - V$, $T - S$, and $P - h$ diagrams of the Carnot cycle are shown in figures 5.14 (a), (b) and (c) respectively.

Being a reversible cycle, the Carnot cycle is the most efficient cycle operating between two specified temperature limits T_L and T_H . Even though the Carnot cycle cannot be achieved in

reality, the efficiency of actual cycles can be improved by attempting to approximate the Carnot cycle more closely.

Thermal Efficiency of Carnot Cycle

Since all the processes that constitute a Carnot cycle are reversible and therefore the Carnot cycle is reversible cycle, the thermal efficiency of a Carnot cycle or Carnot engine is given by

$$\eta_{Carnot} = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Net work output}}{\text{Total heat input}} = \frac{W_{net,output}}{Q_H} \quad \dots\dots\dots(5.100)$$

As there are no heat interactions along the isentropic compression and expansion processes, applying first law of thermodynamics for the complete cycle to get

$$W_{net,output} = Q_H - Q_L \quad \dots\dots\dots(5.101)$$

Then, the Carnot efficiency in terms of heat ratio is derived as

$$\eta_{Carnot} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \quad \dots\dots\dots(5.102)$$

Now, using second law of thermodynamics for the control mass undergoing the cyclic process which is reversible,

$$\oint dS_{CM} = \oint \sum \left(\frac{\delta Q_i}{T_i} \right)_{CM}$$

$$\Rightarrow 0 = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

$$\Rightarrow \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad \dots\dots\dots(5.103)$$

Applying this relation in equation (5.102), the Carnot efficiency can be expressed in terms of temperature ratio as

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H} \quad \dots\dots\dots(5.104)$$

From equation (5.104) it can be concluded that the efficiency of a Carnot cycle is independent of the working substance and depends upon the temperatures of source and sink. The efficiency increases with an increase in source temperature and a decrease in sink temperature.

Carnot cycle is practically impossible

The Carnot cycle gives the maximum possible thermal efficiency, even though it is not practically possible due to the following reasons:

- All the four processes have to be reversible. This needs that there should not involve any kind of frictions within the system (between working fluid particles) as well as between the piston and cylinder walls.
- The reversible heat addition and rejection have to take place with infinitesimal temperature differences. However, the smaller the temperature difference between two systems, the smaller the heat transfer rate will be. Hence, any significant heat transfer through a small temperature difference requires a very large surface area of the cylinder and a very long time which is impractical and not economically feasible.
- For achieving isothermal heat transfer, the piston movement is required to be very slow. However, the piston must move fast for the adiabatic process so that there is less time available for the heat transfer. A variation in the speed of the piston during different processes of a cycle is rather impossible [2].

Thus, Carnot cycle is not practically possible. However, it serves as a reference standard of perfection against which the performance of any practical heat engine cycles can be compared.

5.8.2. Heat Engine

We know that work can be converted to heat directly and completely, but converting heat to work requires the use of some special devices. These devices are called *heat engines*. A heat engine is therefore a thermodynamic device which operates in a cyclic process and is used for continuous conversion of heat energy into mechanical work. Both heat and work interactions take place across the boundary of this cyclic device. It can be executed either in a closed system like cylinder piston device or a steady-flow (open) system like steam power plant. A heat engine cycle operates between two limiting temperatures. The high temperature results from the combustion process in the steam generator or within the cylinder. The low temperature results from the cooling process in the atmosphere or rivers, oceans, lakes etc.. Therefore, a heat engine can be characterized by the following features:

- Heat addition or reception from a high-temperature reservoir or source (solar energy, oil furnace, nuclear reactor, combustion chamber etc.).

- Partial conversion of this heat to mechanical work (usually in the form of a rotating shaft).
- Rejection of the remaining waste heat to a low-temperature reservoir or sink (the atmosphere, rivers, oceans, lakes etc.).
- Operating on a cycle.

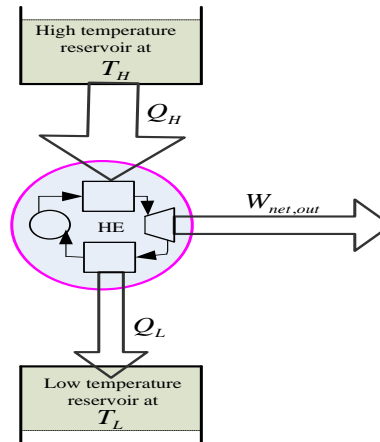


Figure 5.15. Schematic representation of a heat engine [3]

Figure 5.15 shows a schematic representation of a heat engine which receives Q_H amount of heat from a high temperature reservoir at T_H or source and converts some part of it into work ($W_{net,out}$) and rejects remaining waste part Q_L to a low temperature reservoir at T_L or sink.

The fraction of the heat input that is converted to net work output is a measure of the performance of a heat engine and is called the *thermal efficiency*. For heat engines, the desired output is the net work output (i.e. difference between the total work output of the cycle and the total work input) and the required input is the amount of heat supplied to the working fluid. Then, the thermal efficiency of a heat engine is given by

$$\eta_{HE} = \frac{W_{net,output}}{Q_H} \dots\dots\dots(5.105)$$

Applying first law of thermodynamics for a cyclic process,

$$\oint \delta Q = \oint \delta W$$

$$\therefore Q_H - Q_L = W_{net,out} \dots\dots\dots(5.106)$$

Now, using this relation the thermal efficiency of a heat engine can be expressed in terms of heat ratio as

$$\eta_{HE} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \quad \dots\dots\dots (5.107)$$

Thus, the thermal efficiency of a heat engine is always less than unity since both Q_H and Q_L are defined as positive quantities. Now, applying second law of thermodynamics for the cyclic process,

$$\oint dS_{CM} \geq \oint \sum \left(\frac{\delta Q_i}{T_i} \right)_{CM} \quad \dots\dots\dots (5.108)$$

For a complete cycle the change in entropy is always zero because entropy is a property of the system, i.e.

$$0 \geq \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \quad \dots\dots\dots (5.109)$$

For a reversible heat engine, equation (5.109) becomes

$$0 = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

or, $\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$

$$\therefore \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad \dots\dots\dots (5.110)$$

Since equation (5.110) is valid only for a reversible heat engine and by substituting this equation in equation (5.107), thermal efficiency of a reversible heat engine which is also called the *Carnot efficiency* can also be expressed in terms of temperature ratio as

$$\eta_{Carnot} = \eta_{HE,rev} = 1 - \frac{T_L}{T_H} \quad \dots\dots\dots (5.111)$$

Similarly, for an irreversible heat engine, equation (5.109) reduces to

$$0 > \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \quad \dots\dots\dots (5.112)$$

For the same heat input if irreversibility in any heat engine increases, then net work output decreases. This is because of frictional losses and then increase in the heat rejection Q_L . Hence, for an irreversible heat engine, the expression at the right hand side of the equation (5.112) becomes always negative.

Since the net work output from an actual heat engine decreases with the increase in irreversibility, efficiency of an actual heat engine (irreversible heat engine) is always less than that of a reversible heat engine, i.e.

$$\eta_{HE,irrev} < 1 - \frac{T_L}{T_H} \quad \dots\dots\dots (5.113)$$

Combining equations (5.111) and (5.113) yields

$$\eta_{HE} \leq 1 - \frac{T_L}{T_H} \quad \dots\dots\dots (5.114)$$

This is a general equation for the thermal efficiency of a heat engine operating under reversible and irreversible cycles where equal sign is for reversible heat engine and inequality sign is for irreversible heat engine.

5.9. Heat Pump and Refrigerator

It is obvious from experience that heat is transferred in the direction of decreasing temperature, i.e. from high-temperature system to low temperature ones. This heat transfer process occurs in nature without requiring any devices. The reverse process, however, cannot occur by itself. The transfer of heat from a low-temperature system to a high-temperature one requires special devices called heat pumps or refrigerators.

5.9.1. Heat Pump

A heat pump is a device operating on a cyclic process which receives heat from a low temperature reservoir at T_L or surroundings and delivers it to a high temperature reservoir T_H or desired space with the expense of external work. The objective of a heat pump is to maintain the temperature of a desired space (heated space) higher than that of the surroundings. This is accomplished by absorbing heat from a low-temperature source, such as cold outside air in winter, and supplying this heat to the high-temperature desired space such as a house. Figure (5.16) shows a schematic representation of a heat pump as an example to extract heat energy from the cold outdoors and carry it into the warm indoors.

The measure of performance of a heat pump or a refrigerator is expressed in terms of the *coefficient of performance* (COP), which is defined as the ratio of desired effect and the work input as

$$COP = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Desired effect}}{\text{Work input}} \quad \dots\dots\dots(5.115)$$

In case of a heat pump, desired effect is the amount of heat supplied to the desired space (Q_H), i.e.

$$(COP)_{HP} = \frac{Q_H}{W_{in}} \quad \dots\dots\dots (5.116)$$

Using first law of thermodynamics for the heat pump,

$$\oint \delta Q = \oint \delta W$$

$$-Q_H + Q_L = -W_{in}$$

$$\therefore W_{in} = Q_H - Q_L \quad \dots\dots\dots (5.117)$$

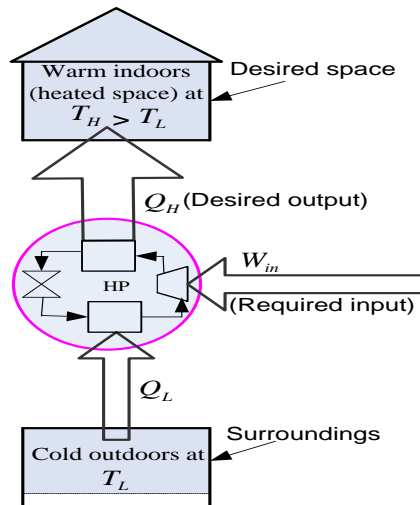


Figure 5.16. Schematic representation of a heat pump as an example to extract heat energy from the cold outdoors and carry it into the warm indoors [3]

Combining equations (5.116) and (5.117) to get

$$(COP)_{HP} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}} \quad \dots\dots\dots (5.118)$$

This equation is valid for both reversible and irreversible heat pumps. Now, applying second law of thermodynamics for the cyclic process,

$$\oint dS_{CM}(=0) \geq \oint \sum \left(\frac{\delta Q_i}{T_i} \right)_{CM}$$

$$\therefore 0 \geq -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \quad \dots\dots\dots (5.119)$$

For a reversible heat pump, equation (5.119) can be written as

$$0 = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L}$$

or, $\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$

$$\therefore \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad \dots\dots\dots (5.120)$$

Since equation (5.120) is valid only for a reversible heat pump and by substituting this equation in equation (5.118), coefficient of performance (COP) for a reversible heat pump can also be expressed in terms of temperature ratio as

$$(COP)_{HP,rev} = \frac{1}{1 - \frac{T_L}{T_H}} = \frac{T_H}{T_H - T_L} \quad \dots\dots\dots (5.121)$$

For the same heating effect Q_H , the work input for an irreversible heat pump should be increased to overcome the frictional losses and therefore, coefficient of performance (COP) of the heat pump decreases. Hence, COP of an irreversible heat pump is always less than that of a reversible heat pump, i.e.

$$(COP)_{HP,irrev} < \frac{T_H}{T_H - T_L} \quad \dots\dots\dots (5.122)$$

Combining equations (5.121) and (5.122) to yield

$$(COP)_{HP} \leq \frac{T_H}{T_H - T_L} \quad \dots\dots\dots (5.123)$$

This is a general equation for the coefficient of performance (COP) of a heat pump operating under reversible and irreversible cycles where equal sign is for reversible heat pump and inequality sign is for irreversible heat pump.

5.9.2. Refrigerator

Another device that transfers heat from a low-temperature system to a high-temperature one is the *refrigerator*. Refrigerator operates on the same cycle as heat pump but differs in its objective. The objective of a refrigerator is to maintain the refrigerated space (desired space) at a low temperature by removing heat from it to a high temperature system (surroundings).

Hence, a refrigerator is a device operating on a cyclic process which receives heat from a low temperature reservoir at T_L or desired space and delivers it to a high temperature reservoir T_H or surroundings with the expense of external work as shown in figure (5.17) which is a schematic representation of a refrigerator.

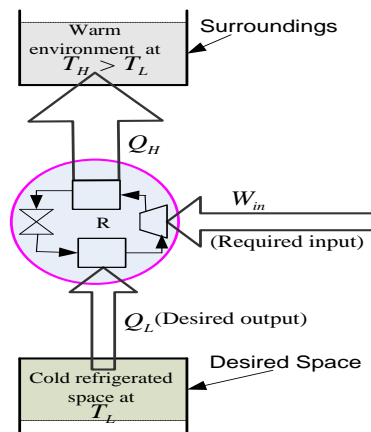


Figure 5.17. Schematic Representation of a Refrigerator [3]

The efficiency or performance of a refrigerator is expressed in terms of the *coefficient of performance* and denoted by $(COP)_R$. The objective of a refrigerator is to remove heat Q_L (desired effect), from the refrigerated or desired space. To accomplish this objective, it requires a work input of W_{in} . Then the COP of a refrigerator can be expressed as

$$(COP)_R = \frac{Q_L}{W_{in}} \dots\dots\dots (5.124)$$

Applying first law and second law of thermodynamics in the similar manner as in the case of a heat pump, the COP of a refrigerator can be derived as

$$(COP)_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} \dots\dots\dots (5.125)$$

This equation is valid for both reversible and irreversible refrigerators. Then, COP for a reversible refrigerator can also be expressed in terms of temperature ratio as done in case of heat pump (equation (5.120)) as

$$(COP)_{R,rev} = \frac{1}{\frac{T_H}{T_L} - 1} = \frac{T_L}{T_H - T_L} \dots\dots\dots (5.126)$$

For the same cooling effect Q_L , the work input for an irreversible refrigerator should be increased to overcome the frictional losses and therefore, coefficient of performance (COP) of the heat pump decreases. Thus, COP of an irreversible refrigerator is always less than that of a reversible refrigerator, i.e.

$$(COP)_{R,irrev} < \frac{T_L}{T_H - T_L} \dots\dots\dots (5.127)$$

Combine equations (5.126) and (5.127) to yield

$$(COP)_R \leq \frac{T_L}{T_H - T_L} \dots\dots\dots (5.128)$$

This is a general equation for the coefficient of performance (COP) of a refrigerator operating under reversible and irreversible cycles where equal sign is for reversible refrigerator and inequality sign is for irreversible refrigerator.

For fixed values of Q_L and Q_H , a comparison of equations (5.118) and (5.125) reveals that

$$COP_{HP} = COP_R + 1 \dots\dots\dots (5.129)$$

This relation implies that the coefficient of performance of a heat pump is always greater than unity since COP_R is a positive quantity.

5.10. Clausius Inequality, Kelvin – Planck and Clausius Statements of Second Law of Thermodynamics and their Equivalence

5.10.1. Clausius Inequality

As derived earlier, from the second of thermodynamics the change in entropy for a control mass with a single heat transfer reservoir as its surroundings is given by

$$dS \geq \frac{\delta Q}{T} \quad \dots \dots \dots (5.130)$$

where equal sign is used for a reversible process and inequality sign is for an irreversible process.

Taking cyclic integral of equation (5.130) for a complete cycle (power or refrigeration cycle), it becomes

$$\oint dS \geq \oint \left(\frac{\delta Q}{T} \right) \quad \dots \dots \dots (5.131)$$

For a complete power or refrigeration cycle the change in entropy is always zero because entropy is an extensive property of the system. Then equation (5.131) reduces to

$$0 \geq \oint \left(\frac{\delta Q}{T} \right) \quad \dots \dots \dots (5.132)$$

From this equation it can be concluded that for both power and refrigeration cycles, the cyclic integral $\oint \left(\frac{\delta Q}{T} \right)$ is zero if the cycle is reversible and less than zero or negative if the cycle is irreversible. This statement with reference to equation (5.132) is also known as *Clausius inequality*. Furthermore, a cycle in which the cyclic integral $\oint \left(\frac{\delta Q}{T} \right)$ is greater than zero violates the second law of thermodynamics and is therefore impossible. Hence, for any cycle if

$$\begin{aligned} \oint \left(\frac{\delta Q}{T} \right) < 0, & \quad \text{then the cycle is irreversible.} \\ \oint \left(\frac{\delta Q}{T} \right) = 0, & \quad \text{then the cycle is reversible.} \\ \oint \left(\frac{\delta Q}{T} \right) > 0, & \quad \text{then the cycle is impossible.} \quad \dots \dots \dots (5.133) \end{aligned}$$

Thus, Clausius inequality not only gives mathematical expression to the second law of thermodynamics, but also throws light on irreversibility of the system.

5.10.2. Classical Statements of Second Law of Thermodynamics and their Equivalence

The second law of thermodynamics has a main feature which describes the possible direction of a process with reference to the system property entropy. The possible direction of a process can also be defined by some popular statements without using the system property entropy. These statements are called classical statements of second law of thermodynamics and described briefly here below.

5.10.2.1. Kelvin - Planck Statement

As demonstrated earlier with reference to the heat engine that even under ideal conditions, a heat engine must reject some heat to a low-temperature reservoir in order to complete the cycle. That means no heat engine can convert all the heat received by it to useful work. This limitation on the thermal efficiency of heat engines forms the basis for the Kelvin–Planck statement of the second law of thermodynamics, which is expressed as follows:

It is impossible to construct a device that operates on a cycle to convert all the heat supplied to it into an equivalent amount of work [1].

Hence, a heat engine must exchange heat with a low-temperature sink as well as a high-temperature source to keep operating. The Kelvin–Planck statement can also be expressed as *no heat engine can have a thermal efficiency of 100 percent*. This impossibility of having a 100 percent efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines. The schematic diagram of the Kelvin - Planck statement is shown in figure (5.18).

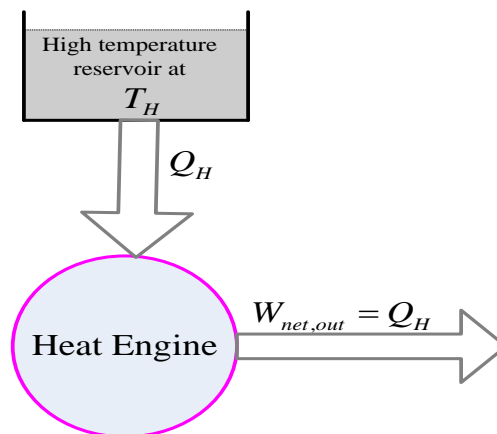


Figure 5.18. Impossible device (heat engine) as defined by Kelvin Planck statement [3]

5.10.2.2. Clausius Statement

The other classical statement of the second law of thermodynamics is known as Clausius statement which is related to refrigerators or heat pumps. The Clausius statement is expressed as follows:

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature system to a higher-temperature system [1].

It is common knowledge that heat does not transfer from a cold system to a warmer one without using any device. The Clausius statement does not imply that a cyclic device that transfers heat from a cold system to a warmer one is impossible to construct. It simply states that such a cyclic device cannot operate unless and until an external work input is supplied to it. The schematic diagram of the Clausius statement is shown in figure (5.19).

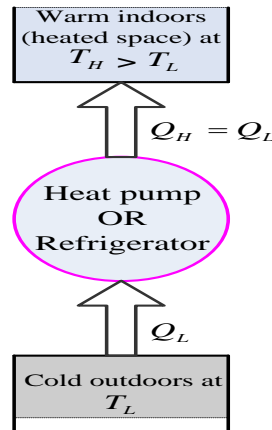


Figure 5.19. Impossible device (heat pump or refrigerator) as defined by Clausius statement [3]

5.10.2.3. Equivalence of Kelvin-Planck and Clausius Statements

The Kelvin–Planck and the Clausius statements are equivalent in their consequences, and either statement can be used as the expression of the second law of thermodynamics. Any device that violates the Kelvin–Planck statement also violates the Clausius statement, and vice versa. This can be demonstrated as follows:

Violation of Kelvin-Planck Statement Resulting in Violation of Clausius Statement

Let us consider a heat engine and heat pump (or refrigerator) combination operating between the same two reservoirs as shown in figure 5.21(a). The heat engine is assumed to have, in violation of the Kelvin–Planck statement, a thermal efficiency of 100 percent, and therefore it converts all the heat Q_H received by it to work W . This work is now supplied to a heat pump or refrigerator

that removes heat in the amount of Q_L from the low-temperature reservoir and rejects heat in the amount of $(Q_H + Q_L)$ to the high-temperature reservoir. During this process, the high temperature reservoir receives a net amount of heat Q_L (the difference between $Q_H + Q_L$ and Q_H). The combination of these two devices constitutes a composite system which can be viewed as a heat pump or a refrigerator as shown in figure 5.21(b), that transfers heat in an amount of Q_L from a cooler system to a warmer one without requiring any work input from outside. This is clearly a violation of the Clausius statement. Therefore, a violation of the Kelvin–Planck statement results in the violation of the Clausius statement.

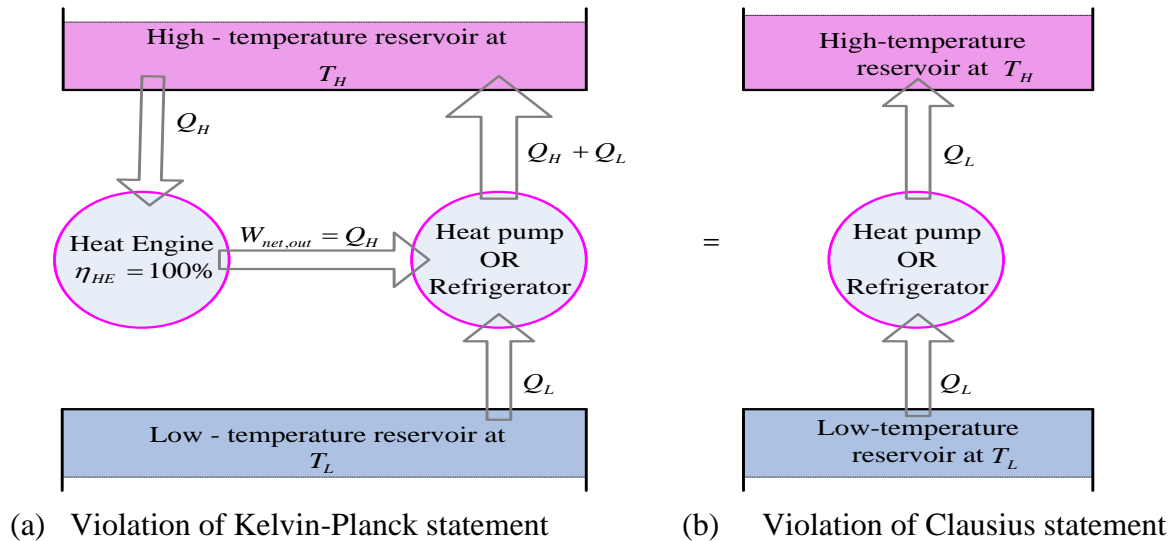


Figure 5.21. Proof that the violation of Kelvin-Planck statement leads to the violation of Clausius statement [3]

Violation of Clausius Statement Resulting in Violation of Kelvin-Planck Statement

Let us consider a heat pump or refrigerator that operates in a cycle and transfers heat of amount Q_L from a low temperature reservoir at T_L to a high temperature reservoir at T_H without any work input from surroundings as shown in figure 5.22(a). This is in violation of the Clausius statement. A heat engine is indicated along with it which also operates in a cycle. This heat engine takes heat of amount Q_H from the high temperature reservoir, delivers $(Q_H - Q_L)$ amount of work to the surroundings and rejects the remaining heat of amount Q_L to the low temperature reservoir. Thus, the heat engine satisfies the Kelvin-Planck statement.

The heat and work interactions for the heat pump (or refrigerator) and heat engine when coupled together are illustrated in figure 5.22(b). This composite system constitutes a device like a heat engine having thermal efficiency 100% that receives $(Q_H - Q_L)$ amount of heat from the high temperature reservoir and converts it completely into an equivalent amount of work $W = (Q_H - Q_L)$ without rejecting any heat to the low temperature reservoir. This operation of the

composite system is in violation of the Kelvin-Planck statement. Thus, violation of Clausius statement leads to violation of Kelvin-Planck statement also.

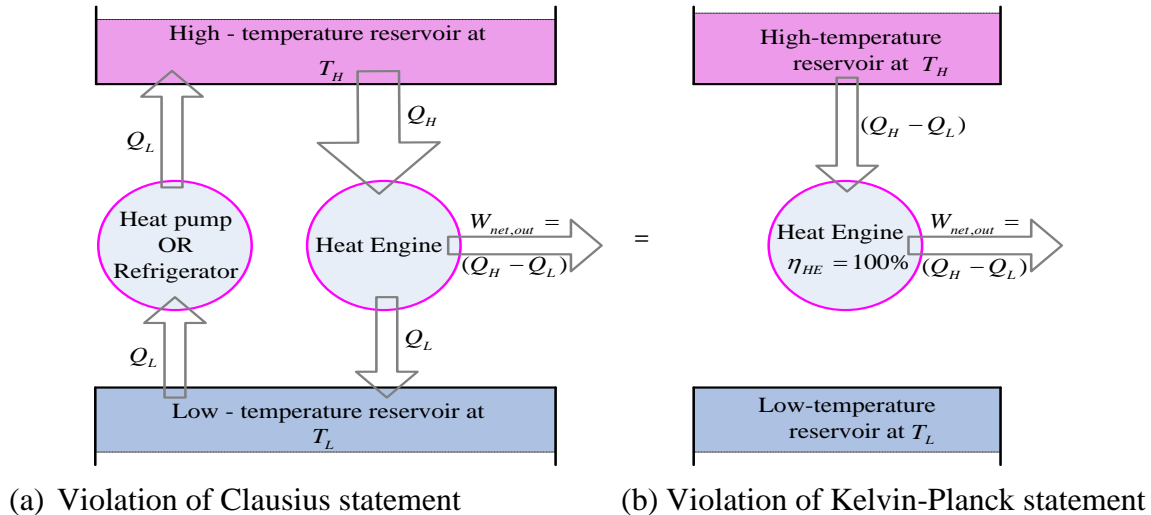


Figure 5.22. Violation of Clausius statement leads to the violation of Kelvin-Planck statement [3]

Lecture Highlights

Carnot cycle: It is an ideal theoretical cycle with efficiency equal to that of a reversible cycle. This cycle is practically not possible to realize but it is used as reference standard to compare the performances of different practical cycles. Carnot cycle consists of four processes namely:

- (i) isothermal heat addition,
- (ii) isentropic expansion,
- (iii) isothermal heat rejection and
- (iv) isentropic compression.

The Carnot cycle gives the maximum possible thermal efficiency, even though it is not practically possible due to the following reasons:

- All the four processes have to be reversible. This needs that there should not involve any kind of frictions within the system (between working fluid particles) as well as between the piston and cylinder walls.
- The reversible heat addition and rejection have to take place with infinitesimal temperature differences. However, the smaller the temperature difference between two systems, the smaller the heat transfer rate will be. Hence, any significant heat transfer through a small temperature difference requires a very large surface area of the cylinder and a very long time which is impractical and not economically feasible.

- For achieving isothermal heat transfer, the piston movement is required to be very slow. However, the piston must move fast for the adiabatic process so that there is less time available for the heat transfer. A variation in the speed of the piston during different processes of a cycle is rather impossible.
- *Efficiency*: It is defined as the ratio of desired output (work output) to the required input (heat supplied), i.e.

$$\eta = \frac{\text{Desired output}}{\text{Required input}}$$

- *Heat engine*: It is a device which operates on a cyclic process and converts heat energy into mechanical work. The efficiency of heat engine is the ratio of work output to the heat supplied and can be derived for both reversible or irreversible heat engines as

$$\eta_{HE} = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

Using second law of thermodynamics for reversible heat engine,

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

The efficiency of a reversible heat engine which is also called a *Carnot efficiency* is given by

$$\eta_{HE,rev} = \eta_{Carnot} = 1 - \frac{T_L}{T_H}.$$

As the work output from the real engine decreases with increase in irreversibility, efficiency of a real engine (or irreversible engine) is always less than that of reversible engine, i.e.

$$\eta_{HE,irrev} < \left(1 - \frac{T_L}{T_H}\right)$$

- *Heat pump*: It is a device operating on a cyclic process which transfers heat from a low temperature reservoir (surroundings) to a high temperature reservoir (desired space) with the aid of external work. It maintains the temperature of a desired space higher than that of the surroundings thereby providing the heating effect.
- *Coefficient of performance (COP)*: It is defined as the ratio of desired effect (heating or cooling) to the work supplied, i.e.

$$\text{COP} = \frac{\text{Desired effect}}{\text{Work input}}$$

- For heat pump (reversible or irreversible), desired effect is the amount of heat supplied to desired space (Q_H) and therefore COP is given by

$$(\text{COP})_{HP} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L}$$

Using second law of thermodynamics for reversible heat pump,

$$\frac{Q_L}{T_L} - \frac{Q_H}{T_H} = 0$$

The COP of a reversible heat pump is given by

$$(COP)_{HP,rev} = \frac{T_H}{T_H - T_L}.$$

As the work input to the real heat pump should be increased with increase in irreversibility for the same heating effect, COP of a real heat pump (or irreversible heat pump) is always less than that of reversible heat pump, i.e.

$$(COP)_{HP,irrev} < \frac{T_H}{T_H - T_L}.$$

- *Refrigerator*: It is a device operating on a cyclic process which transfers heat from a low temperature reservoir (desired space) to a high temperature reservoir (surroundings) with the aid of external work. It maintains the temperature of a desired space lower than that of the surroundings thereby providing the cooling effect.
- *For refrigerator (reversible or irreversible)*, desired effect is the amount of heat taken out from desired space (Q_L) and therefore COP is given by

$$(COP)_R = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

Using second law of thermodynamics for reversible refrigerator,

$$\frac{Q_L}{T_L} - \frac{Q_H}{T_H} = 0$$

The COP of a reversible refrigerator is given by

$$(COP)_{R,rev} = \frac{T_L}{T_H - T_L}.$$

As the work input to the real refrigerator should be increased with increase in irreversibility for the same cooling effect, COP of a real refrigerator (or irreversible refrigerator) is always less than that of reversible refrigerator, i.e.

$$(COP)_{R,irrev} < \frac{T_L}{T_H - T_L}$$

For the same machine, it reveals: $(COP)_{HP} - (COP)_R = 1$.

- *Similarities between heat pump and refrigerator are:*
 1. Cycle execution direction of both devices is same and it is opposite to that of heat engine.
 2. Both devices work on the vapor compression refrigeration cycle and have same cycle components, e.g. compressor, condenser, expansion valve (throttling valve) and evaporator.
 3. Both devices need external work for the execution of cycle.
 4. Net work of cycle is negative as both are refrigeration cycles.
 5. Working substance is a refrigerant in both devices.
 6. Both devices transfer heat from low temperature reservoir (sink) to the high temperature reservoir (source).
 7. Performance of both devices is measured by their COP which is greater than unity.

➤ *Differences between heat pump and refrigerator are:*

Heat Pump	Refrigerator
1. Its main purpose is to heat the desired space (room during winter season). 2. It absorbs heat from the atmosphere which is at low temperature and throws it to desired space that is to be heated and is at high temperature. 3. In heat pump the evaporator is located outside the room (desired space) which is to be heated. 4. The condenser in heat pump is located inside the room (desired space) and it acts as heating device. 5. In heat pump, condenser performs main function of heating the room while the evaporator absorbs heat from the atmosphere. 6. COP of heat pump is higher than that of refrigerator and is given by $(COP)_{HP} = \frac{Q_H}{W} = 1 + (COP)_R$	1. Its purpose is to cool or freeze a substance in desired space (compartment of kitchen refrigerator or freezer). 2. It absorbs heat from the desired space which is to be cooled and is at low temperature and throws it to the atmosphere at high temperature. 3. In refrigerator the evaporator is located inside the freezer (desired space) and it acts as cooling device. 4. The condenser in the refrigerator is located outside the freezer compartment and it is exposed to the atmosphere. 5. In refrigerator, evaporator performs main function of cooling or freezing the desired space while the condenser delivers heat to atmosphere. 6. COP of refrigerator is lower than that of heat pump and given by $(COP)_R = \frac{Q_L}{W} = (COP)_{HP} - 1$

➤ *Clausius Inequality:* For any cycle if

- $\oint \left(\frac{\delta Q}{T} \right) < 0$, then the cycle is irreversible.
- $\oint \left(\frac{\delta Q}{T} \right) = 0$, then the cycle is reversible.
- $\oint \left(\frac{\delta Q}{T} \right) > 0$, then the cycle is impossible.

➤ *Classical statements of second law of thermodynamics:* Those statements with the help of which a direction or possibility of any process can be defined without using the property entropy are called classical statements of second law.

- *Kelvin – Planck statement:* “It is impossible to construct a heat engine operating on a cycle which converts all the heat energy supplied to it into mechanical work”.
- *Clausius statement:* “It is impossible to construct a device operating on a cycle which transfers heat from a body at a lower temperature to a body at a higher temperature without aid of external work”.

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