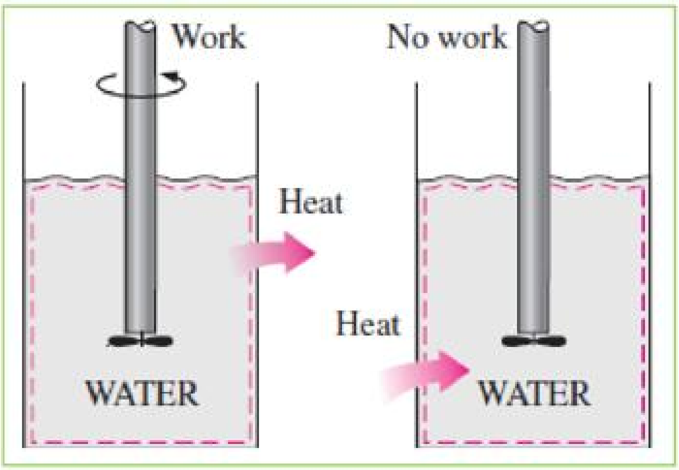
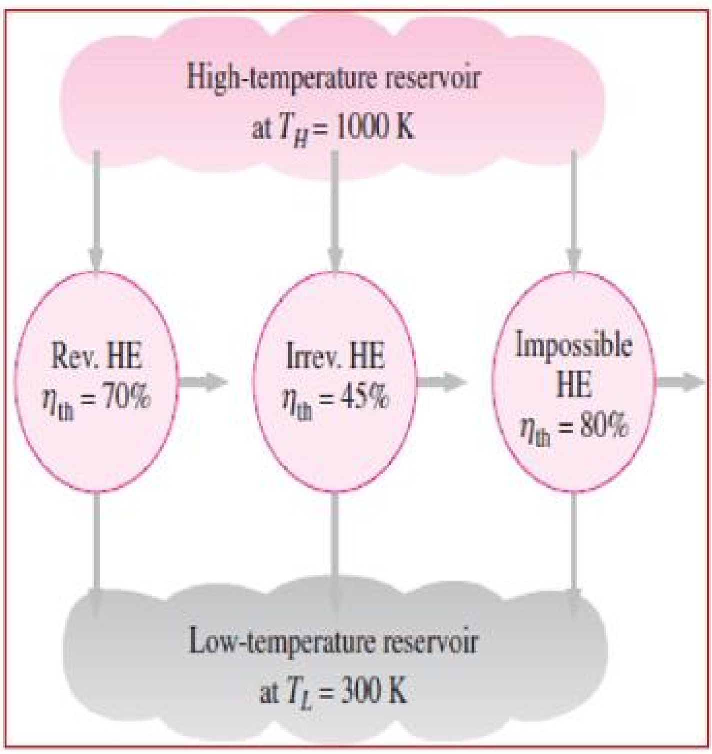
UNIT-II

SECOND LAW OF THERMODYNAMICS





Course Contents

3.1 Introduction

- To this point, we have focused our attention on the first law of thermodynamics, which requires that energy be conserved during a process but this conservation principles do not always suffice, however, and often the second law of thermodynamics is also required for thermodynamic analysis.
- The objective of this chapter is to introduce the second law of thermodynamics which asserts that processes occur in a certain direction and the energy has quality as well as quantity, also any process cannot take place unless it satisfies both the first and second laws of thermodynamics. A number of deductions that may be called corollaries of the second law are also considered, including performance limits for thermodynamic cycles.

3.2 Introducing Second law

As pointed out repeatedly according to conservation of energy principle that, 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.

Below mention examples which satisfy the first law of thermodynamics:

1. It is common experience that a cup of hot coffee left in a cooler room eventually cools off (Fig. 3.1). This process satisfies the first law of thermodynamics since 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.

Fig. 3.1 A cup of hot coffee does not get hotter in a cooler room

2. As another familiar example, consider the heating of a room by the passage of electric current through a resistor (Fig. 3.2). 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.

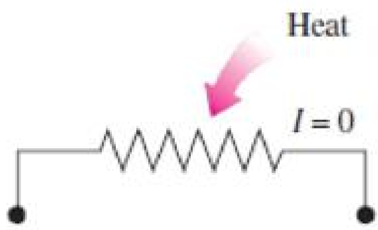


Fig. 3.2 Transferring heat to a wire will not generate electricity

3. Finally, consider a paddle-wheel mechanism that is operated by the fall of a mass (Fig. 3.3). 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.

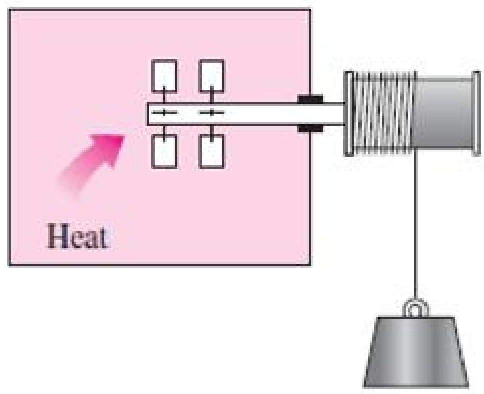


Fig.3.3 Transferring heat to a paddle wheel will not cause it to rotate

4. Consider a running automobile vehicle stopped by applying brakes, and the process changes the kinetic energy of the vehicle in to heat and the brakes get heated up. Thus increase in internal energy of brakes in accordance with the first law. Now cooling of brakes to their initial state never puts the vehicle in to motion. Heat in the brake cannot convert to mechanical work even though that would not violate the principle of energy conversion.
5. Air held at a high pressure p_i in a closed tank would flow spontaneously to the lower pressure surroundings at p_0 if the interconnecting valve were opened, (Fig. 3.4). Eventually fluid motions would cease and all of the air would be at the same pressure as the surroundings. Drawing on experience, it should be clear that the *inverse* process would not take place *spontaneously,* even though energy could be conserved. Air would not flow spontaneously from the surroundings at p_0 into the tank, returning the pressure to its initial value.

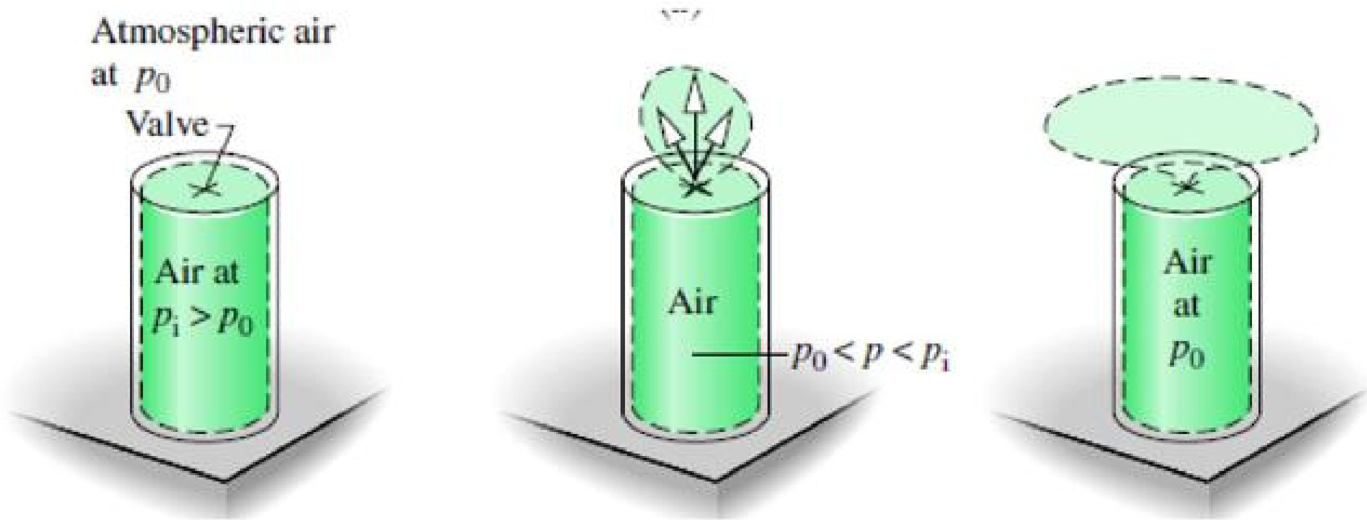


Fig. 3.4 Spontaneous expansion

6. When a block slides down a rough plane, it warmer. However, the reverse process where the block slides up the plane and becomes cooler is not true even though the first law will still hold good.
7. Water flows from a higher level to a lower level, and reverse is not automatically possible. A mechanical energy from an external source would be required to pump the water back from the lower level to higher level.
8. Fuels (coals, diesel, and petrol) burns with air to form the products of combustion. Fuels once burnt cannot be restored back to original from.
9. Persons always grow old…………
10. When hydrogen and oxygen are kept in an isolated system, they produce water on chemical reaction. But the water never dissociates into hydrogen and oxygen again.

It is clear from these above arguments that processes proceed in a certain direction and not in the reverse direction (Fig. 3.5).

Fig. 3.5 Processes occur in a certain direction, and not in the reverse direction

A process cannot take place unless it satisfies both the first and second laws of thermodynamics.

Fig. 3.6 A process must satisfy both the first and second laws of thermodynamics to proceed

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.

3.2.1 Limitations of First Law of Thermodynamics

1. First law fixes the exchange rate between the heat and work, and places no restrictions on the directions of change.

2. Processes proceed spontaneously in certain direction, but revere is not automatically attainable even though the reversal of processes does not violate the first law.
3. First law provides necessary but not sufficient condition for process to be occurs.

3.3 Basic Definitions

3.3.1 Thermal Energy Reservoir

"It is defined as that part of environment which can exchange heat energy with system, it has sufficiently large heat capacity and its temperature is not affected by a quantity of heat transfer to or from it". (Fig. 3.7a)

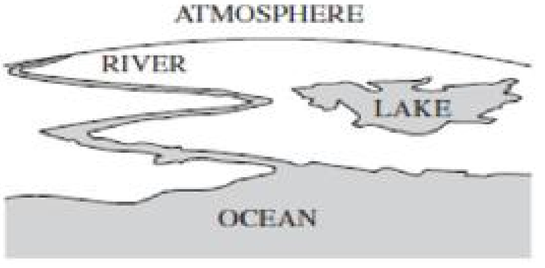


Fig. 3.7 (a) Bodies with relatively large thermal masses can be modelled as thermal energy reservoirs

Heat Source

"It is defined as the thermal reservoir which is at high temperature and supplies heat is called a heat source." i.e. boiler furnace, combustion chamber etc. (Fig. 3.7b)

Heat Sink

"It is defined as the thermal reservoir which is at low temperature and to which heat is transferred is called heat sink". i.e. atmospheric air, ocean, rivers etc. (Fig. 3.7b)

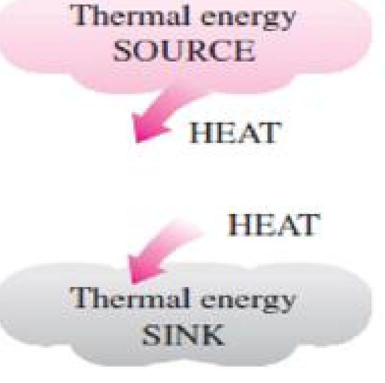


Fig. 3.7 (b) A source supplies energy in the form of heat, and a sink absorbs it

3.3.2 Heat Engine

"It is defined as thermodynamic device used for continuous production of work from heat when operating in a cyclic process is called heat engine".

Characteristics of Heat Engine:

- They receive heat from a high-temperature source at temperature T_1 (i.e solar energy, oil furnace, nuclear reactor, etc.)
- They convert part of this heat to work (usually in the form of a rotating shaft).

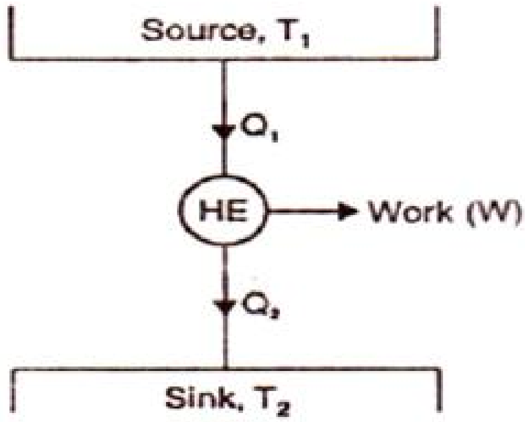


Fig. 3.8 Schematic of energy interaction in heat engine

- They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
- They operate on a cycle. (Fig. 3.8)

Working Fluid

"It is defined as a fluid to and from which heat is transferred while undergoing a cycle is called the working fluid."

Thermal Efficiency

"It is defined as the ratio of the desired net work output to the required heat input is called thermal efficiency."

Thus thermal efficiency of a heat engine can be expressed as,

$$\eta_{th} = \frac{\text{desired work output}}{\text{required heat input}} = \frac{W_{net}}{Q_{in}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

3.3.3 Refrigerator

"It is defined as the mechanical device that used for the transfer of heat from a low-temperature medium to a high-temperature medium is called refrigerator." (Fig. 3.9)

- The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it and discharging this heat to a higher-temperature medium.

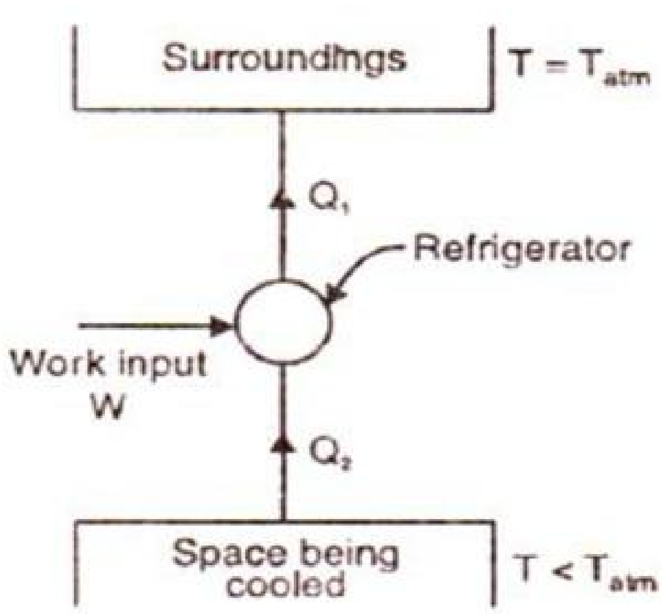


Fig. 3.9 The schematic of energy interaction in refrigerator

Coefficient of Performance of Refrigerator

"The COP of a refrigerator can be expressed as the ratio of refrigerating effect to the work input. "

Mathematically,

$$COP_R = \frac{\text{desired output}}{\text{required input}} = \frac{\text{refrigerating effect}}{\text{work input}} = \frac{Q_2}{W_{net,in}}$$

The conservation of energy principle for a cyclic device requires that,

$$W_{net,in} = Q_1 - Q_2$$

$$COP_R = \frac{Q_2}{Q_1 - Q_2}$$

3.3.4 Heat Pump

"It is defined as the mechanical device that transfers heat from a low-temperature medium to a high-temperature one is called heat pump."

- The objective of heat pump is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low-temperature source, such as well water or cold outside air in winter, and supplying this heat to the high-temperature medium such as a house (Fig. 3.10).

Coefficient of Performance of Heat Pump

"The COP of a heat pump can be expressed as the ratio of heating effect to the work input".

Mathematically,

$$COP_{HP} = \frac{\text{desired output}}{\text{required input}} = \frac{\text{heating effect}}{\text{work input}} = \frac{Q_1}{W_{net,in}}$$

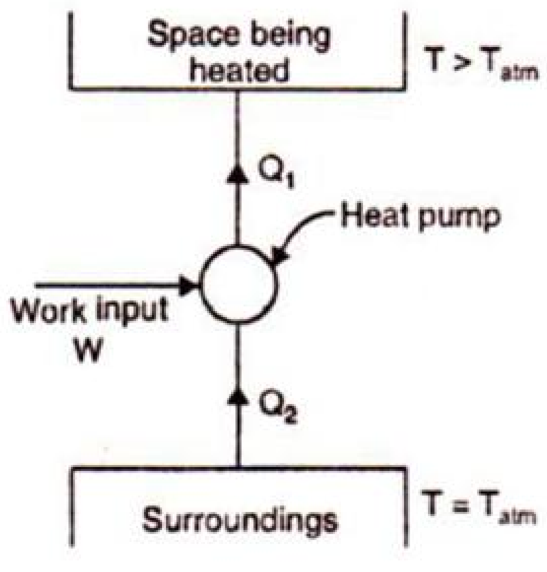


Fig. 3.10 The Schematic of heat pump

The conservation of energy principle for a cyclic device requires that,

$$W_{net,in} = Q_1 - Q_2$$

$$COP_{HP} = \frac{Q_1}{Q_1 - Q_2}$$

3.3.5 Perpetual-Motion Machines (PMM)

"It is defined as the device that violates either law (first or second) is called a perpetual-motion machine." (Fig. 3.11)

PMM1: "A device that violates the first law of thermodynamics (by creating energy) is called a perpetual-motion machine of the first kind (PMM1)."

PMM2: "A device that violates the second law of thermodynamics is called a perpetual-motion machine of the second kind (PMM2)."

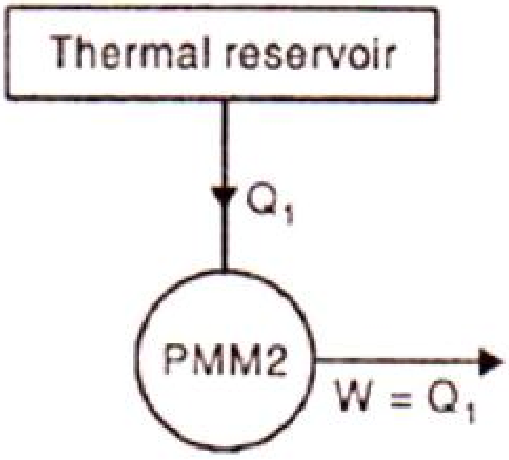


Fig. 3.11 Perpetual motion machine of the second kind

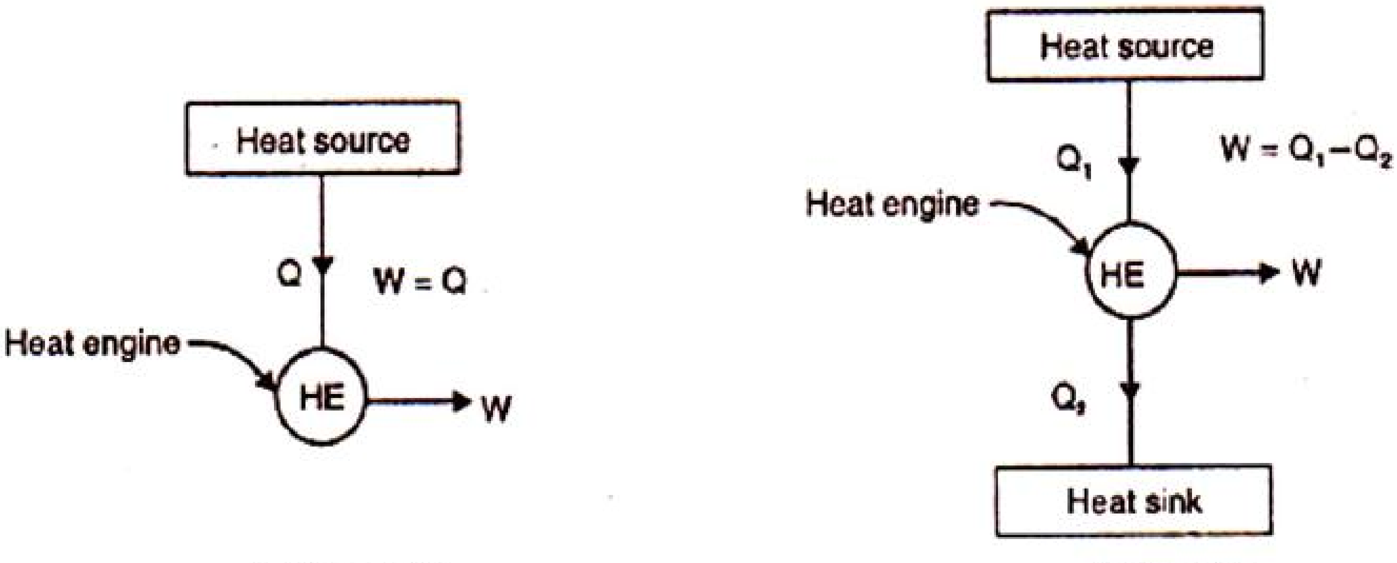
$$\eta_{th} = \frac{W_{net}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

- In above equation, if $Q_2 = 0$, then $W_{net} = Q_1$ and $\eta_{th} = 100\%$. That is, if the engine exchanges heat only with one thermal reservoir (Fig 3.11), then the entire heat supplied to it gets converted into an equivalent amount of work and the efficiency becomes 100%. Such a heat engine is called a PMM2. The PMM2 is in conformity with the first law, but it violates the Kelvin-Planck statement of second law.

3.4 The Statements of Second Law of Thermodynamics

3.4.1 Kelvin–Planck Statement

"It is impossible to construct a device that operates in thermodynamic cycle produce no effect other than work output and exchange heat with a single reservoir". (Fig. 3.12)



(a) Impossible *(b) Possible*

Fig. 3.12 Schematic representation of heat engine accordance with Kelvin–Planck statement

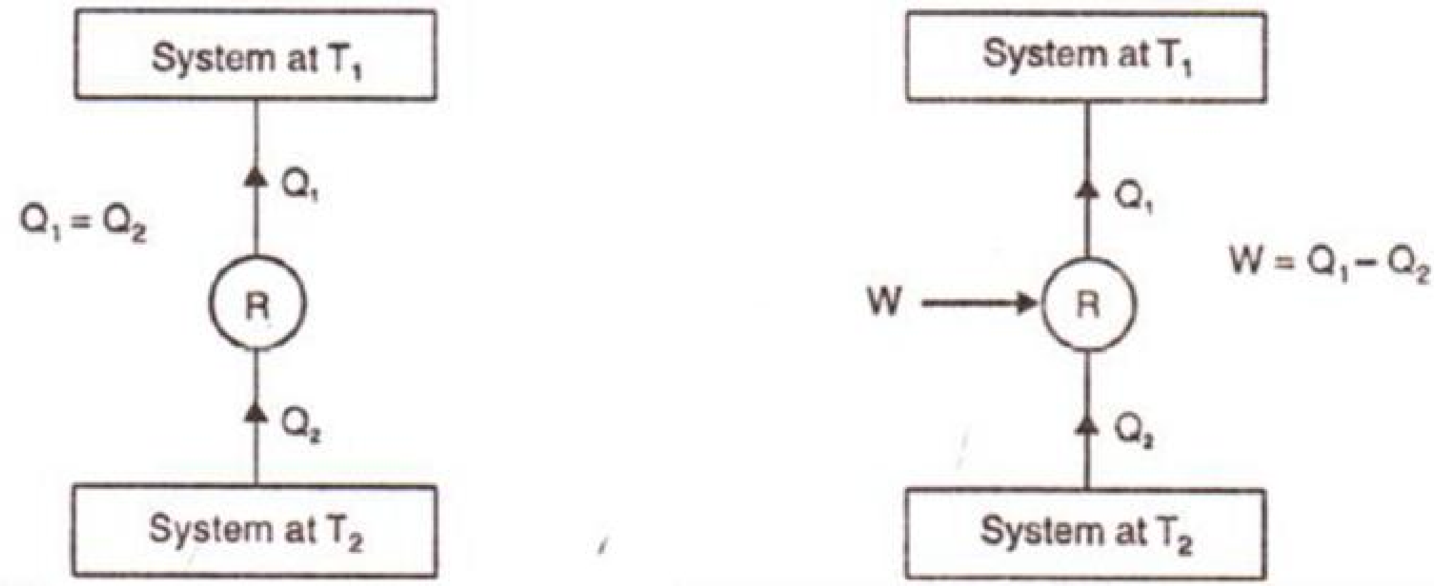
[*Important Note FYI:* a heat engine must exchange heat with a low-temperature sink as well as a high-temperature source to keep operating. Note that the impossibility of having a 100% efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines.]

3.4.2 Clausius Statement

"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 reservoir to a higher-temperature reservoir." (Fig. 3.13)

OR

"It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body."



(a) Impossible *(b) Possible*

Fig. 3.13 Schematic representation of refrigerator accordance with the Clausius statement

[Note FYI: It is common knowledge that heat does not, of its own volition, transfer from a cold medium to a warmer one. The Clausius statement does not imply that a cyclic device that transfers heat from a cold medium to a warmer one is impossible to construct. In fact, this is precisely what a common household refrigerator does. It simply states that a refrigerator cannot operate unless its compressor is driven by an external power source, such as an electric motor.]

3.4.3 Equivalency of the Two Statements

The Kelvin-Planck and Clausius statements, though worded differently, are interlinked and are complementary to each other. It is impossible to have a device satisfying one statement and violating the other. Any device that violates Clausius statement leads to violation of Kelvin-Planck statement and vice-versa.

(a) Violation of Clausius statement leading to violation of Kelvin-Planck statement.

- As shown in Fig. 3.14 (a) a refrigerator R that operates in a cycle and transfers Q_2 amount of heat from low temperature reservoir at T_2 to a high temperature reservoir at T_1 without any work input from external agency (surroundings). This is in violation of the Clausius statement.

- Along with this heat engine E, that also operates in a cycle, takes Q_1 amount of heat from the high temperature reservoir, delivers $Q_1 - Q_2$ amount of work to the surroundings and rejects the remaining Q_2 amount of heat to the low temperature reservoir. The engine operates in conformity with the Kelvin-Planck statement.

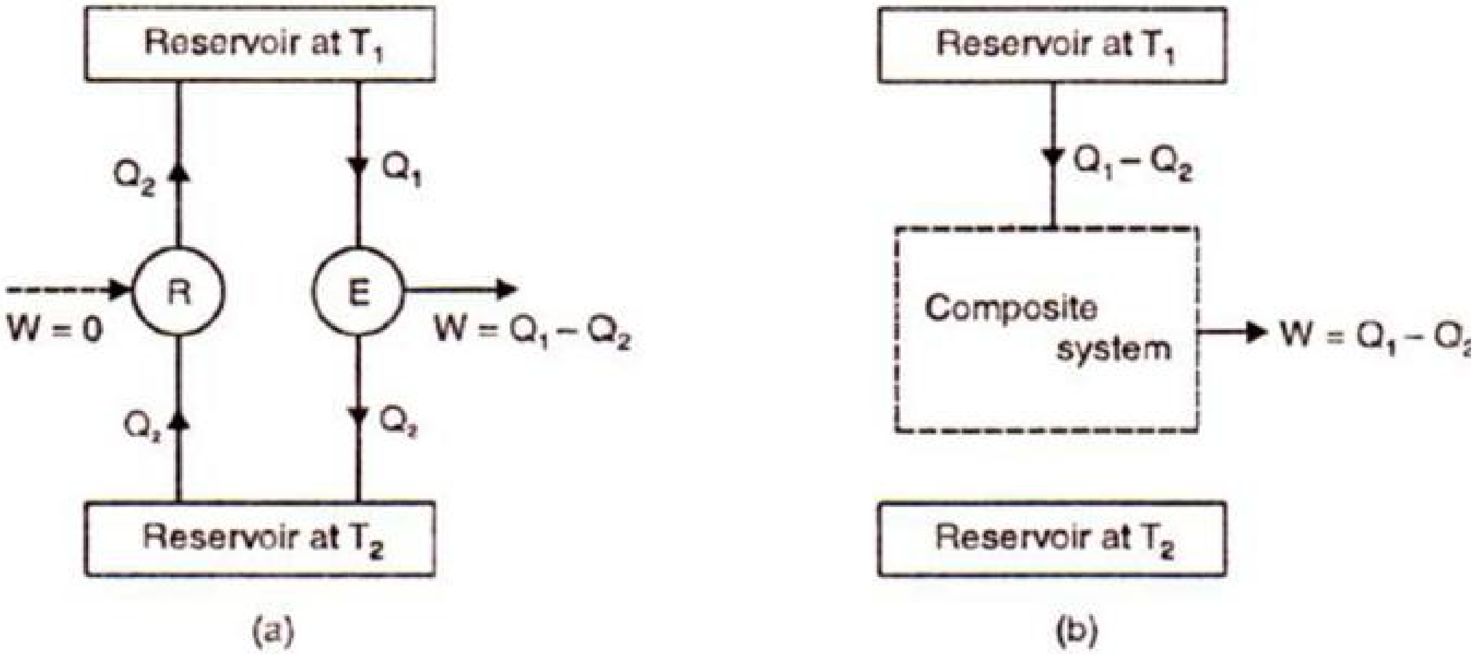


Fig. 3.14 Proof of the violation of the Clausius statement leads to the violation of the Kelvin–Planck statement

- As shown in Fig. 3.14 (b) the heat and work interactions for the refrigerator and heat engine when coupled together. This composite system constitutes a device that receives $Q_1 - Q_2$ amount of heat from the high temperature reservoir and converts it completely into an equivalent amount of work $W = Q_1 - Q_2$ without rejecting any heat to the low temperature reservoir. This operation of the composite system is in violation of the Kelvin-Planck statement.

(b) Violation of Kelvin-Planck statement leading to violation of Clausius statement.

- As shown in Fig. 3.15 (a) an engine E which operates from a single heat reservoir at temperature T_1. It receives Q_1 amount of heat from this reservoir and converts it completely into an equivalent amount of work $W = Q_1$ without rejecting any heat to the low temperature reservoir at T_2. This is in violation with the Kelvin-Planck statement.
- Along with this the refrigerator R which extracts Q_2 amount of heat from the low temperature reservoir, is supplied with Q_1 amount of work from an external agency (surroundings) and supplies $Q_1 + Q_2$ units of heat to the high temperature reservoir. The refrigerator operates in conformity with the Clausius statement.

– As shown in Fig. 3.15 (b) the work and heat interactions for the refrigerator and heat engine when coupled together. The output of the engine is utilized to drive the refrigerator. This composite system constitutes a device which transfers heat from the low temperature reservoir to the high temperature reservoir without any work input from an external agency. This is in violation of the Clausius statement. Thus violation of Kelvin-Planck statement leads to violation of Clausius statement also.

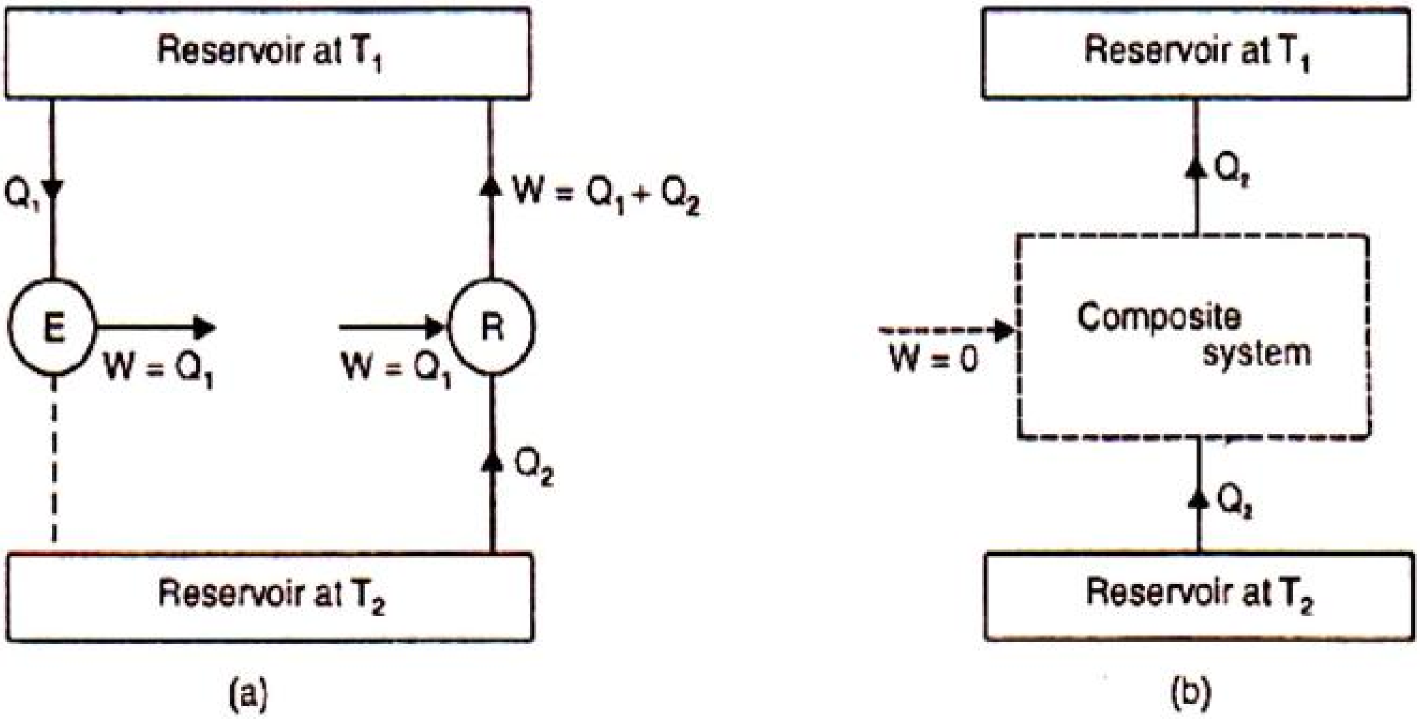


Fig. 3.15 Proof of the violation of the Kelvin–Planck statement leads to the violation of the Clausius statement

Therefore, the Clausius and the Kelvin–Planck statements are two equivalent expressions of the second law of thermodynamics.

3.5 Reversible and Irreversible Process

3.5.1 Reversible Process

Definition: "A *reversible process* is defined as a process that can be reversed without leaving any trace on the surroundings and both the system and the surroundings are restored to their respective initial states by reversing the direction of the process".

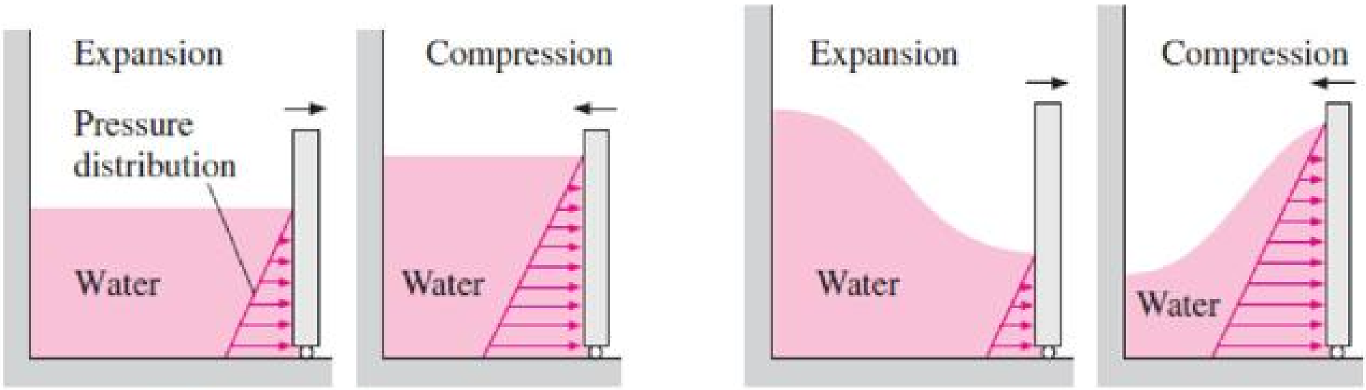
Conditions of Reversible Process

1. The process must proceed in a series of equilibrium states.
2. Heat transfer should not take place with finite temperature difference.
3. The process should be quasi-static and it should proceed at infinitely slow speed.
4. The process should not involve friction of any kind (mechanical and intermolecular)

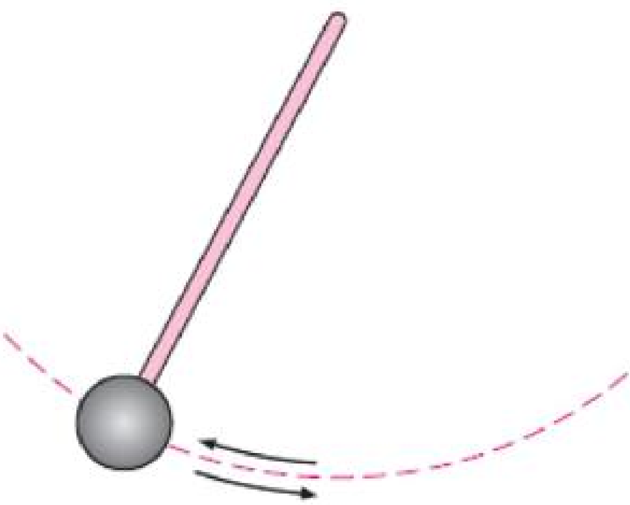
Salient Features

1. It is quasi-static process which can be carried out in the reverse direction along the same path. It can be proceed in either direction without violating the second law of thermodynamics.

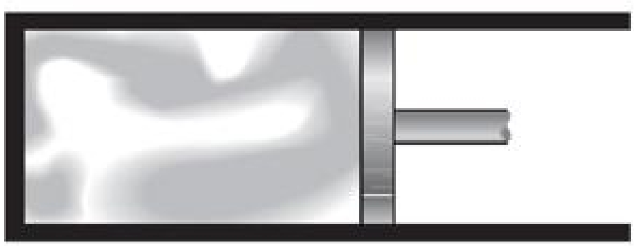
2. The energy transfer as heat and work during the forward process should be identically equal to energy transfer as heat and work during the reversal of the process.
3. It is possible only if the net heat and net work exchange between the system and the surroundings is zero for the combined (original and reverse) process or it leaves no trace or evidence of its occurrence in the system and surroundings.



(*a*) Slow (reversible) process (*b*) Fast (irreversible) process



(*a*) Frictionless pendulum



(*b*) Quasi-equilibrium expansion and compression of a gas

Fig. 3.16 Reversible processes deliver the most and consume the least work

4. Reversible processes can be viewed as theoretical limits for the corresponding irreversible ones.
5. The more closely we approximate a reversible process, the more work delivered by a work-producing device or the less work required by a work-consuming device.
6. It leads to the definition of the second law efficiency for actual processes, which is the degree of approximation to the corresponding reversible processes. This enables us to compare the performance of different devices that are designed to do the same task on the basis of their efficiencies.
7. It is idealized process actually do not occur in nature.
8. There should be no free or unrestricted expansion and no mixing of the fluids.

9. Work done during reversible process is represented by area under process curve on p-v diagram, and is equal to $\int_1^2 pdv$

Some Notable Examples of ideal reversible processes are:

1. Motion without friction.
2. Frictionless adiabatic and isothermal expansion or compression.
3. Restricted and controlled expansion or compression.
4. Elastic stretching of a solid.
5. Restrained discharge of the battery.
6. Electric circuit with zero resistance.
7. Polarisation, magnetisation effects and electrolysis.
8. Condensation and boiling of liquids.

3.5.2 Irreversible Process

Definition: "An *irreversible process* is defined as a process that can be reversed with permanent leaving any trace on the surroundings and both the system and the surroundings are not restored to their respective initial states by reversing the direction of the process".

These processes that occurred in a certain direction, once having taken place, these processes cannot reverse themselves spontaneously and restore the system to its initial state.

- *For example,* once a cup of hot coffee cools, it will not heat up by retrieving the heat it lost from the surroundings. If it could, the surroundings, as well as the system (coffee), would be restored to their original condition, and this would be a reversible process.
- It should be pointed out that a system can be restored to its initial state following a process, regardless of whether the process is reversible or irreversible. But for reversible processes, this restoration is made without leaving any net change on the surroundings, whereas for irreversible processes, the surroundings usually do some work on the system and therefore does not return to their original state.

Salient Features

1. It can be carried out in one direction.
2. It occurs at a finite rate.
3. It cannot be reversed without permanent change in surroundings.
4. The system is in never in equilibrium state at any instant during an irreversible process.

Some Notable Examples of an irreversible process are:

1. Spontaneous chemical reaction.
2. Viscous flow, fluid flow with friction.
3. Inelastic deformation and hysteresis effects.
4. Electric circuit with resistance.

5. Diffusion of gases, mixing of dissimilar gases.
6. Heat transfer takes place with finite temperature difference.
7. Free expansion and throttling process.
8. Friction—sliding friction as well as friction in the flow of fluids

3.5.3 Irreversibilities

Definition: "It is defined as the factors that cause a process to be irreversible are called irreversibilities."

(A) Causes of Irreversibilities

- They include friction, unrestrained expansion, mixing of two fluids, and heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions. The presence of any of these effects renders a process irreversible. A reversible process involves none of these. Some of the frequently encountered irreversibilities are discussed briefly below.

1. Friction:

- When two bodies in contact are forced to move relative to each other (a piston in a cylinder, for example, as shown in Fig. 3.17), a friction force that opposes the motion develops at the interface of these two bodies, and some work is needed to overcome this friction force. The energy supplied as work is eventually converted to heat during the process and is transferred to the bodies in contact, as evidenced by a temperature rise at the interface.

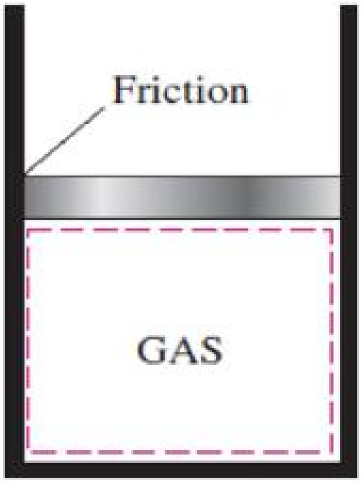


Fig. 3.17 Friction renders a process irreversible

- When the direction of the motion is reversed, the bodies are restored to their original position, but the interface does not cool, and heat is not converted back to work. Instead, more of the work is converted to heat while overcoming the friction forces that also oppose the reverse motion. Since the system (the moving bodies) and the surroundings cannot be returned to their original states, this process is irreversible. Therefore, any process that involves friction is irreversible.

2. Unrestrained expansion:

- Unrestrained expansion of a gas separated from a vacuum by a membrane, as shown in Fig. 3.18. When the membrane is ruptured, the gas fills the entire tank. The only way to restore the system to its original state is to compress it to its initial volume, while transferring heat from the gas until it reaches its initial temperature. From the conservation of energy considerations, it can easily be shown that the amount of heat transferred from the gas equals the amount of work done on the gas by the surroundings.

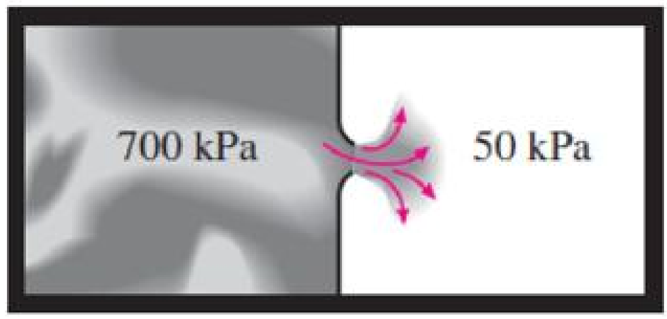


Fig. 3.18 Unrestrained expansion of a gas makes the process Irreversible

- The restoration of the surroundings involves conversion of this heat completely to work, which would violate the second law. Therefore, unrestrained expansion of a gas is an irreversible process.

3. Heat transfer through a finite temperature difference:

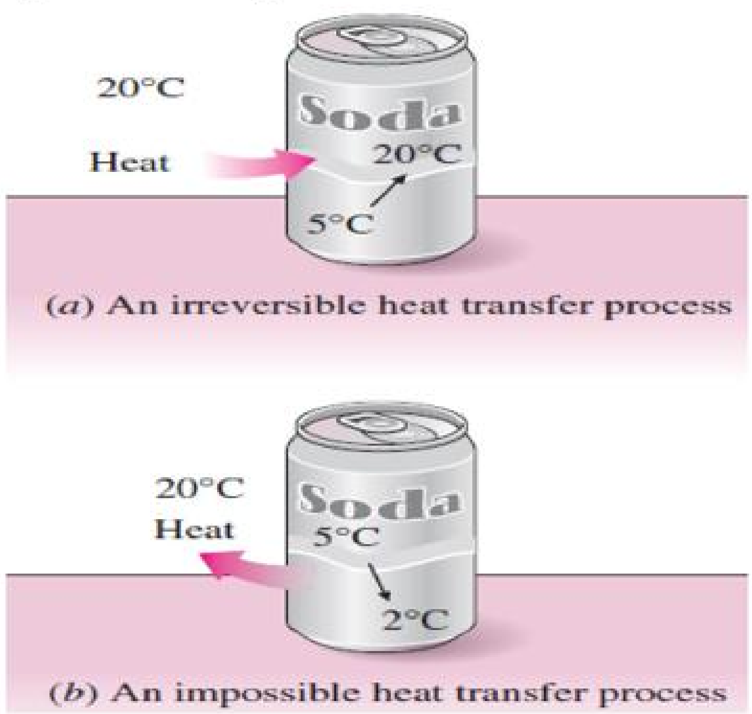


Fig. 3.19 (a) Heat transfer through a temperature difference is irreversible, and (b) the reverse process is impossible

- Consider a can of cold soda left in a warm room Fig. 3.19 (a). Heat is transferred from the warmer room air to the cooler soda. The only way this process can be reversed and the soda restored to its original temperature is to provide refrigeration, which requires some work input. At the end of the reverse process, the soda will be restored to its initial state, but the surroundings will not be. The internal energy of the surroundings will increase by an amount equal in magnitude to the work supplied to the refrigerator. The restoration of the surroundings to the initial state can be done only by converting this excess internal energy completely to work, which is impossible to do without violating the second law.

- Since only the system, not both the system and the surroundings, can be restored to its initial condition, heat transfer through a finite temperature difference is an irreversible process.

(B) Types of Irreversibilities

1. Internally Irreversibilities: These are associated with dissipative effects within working fluid itself.

2. Externally Irreversibilities: These are associated with dissipative effects outside the working fluid or boundaries of the system. i.e. Mechanical friction occurring during process.

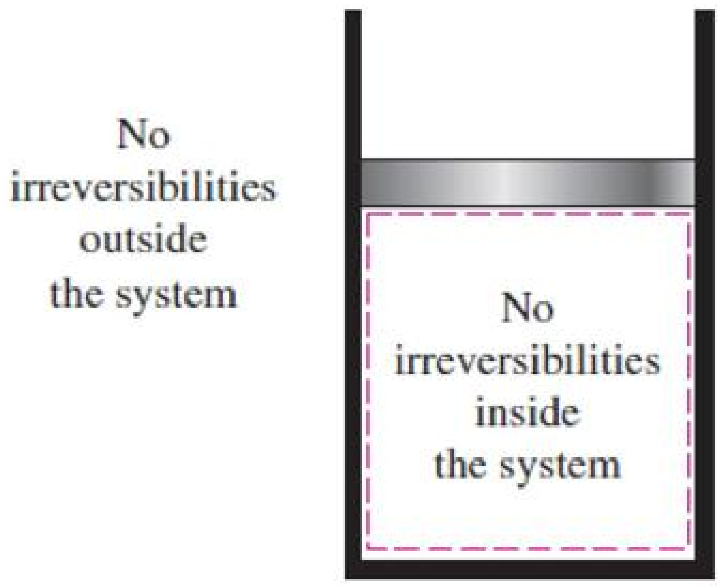


Fig. 3.19 (b) A reversible process involves no internal and external irreversibilities (Totally reversible)

[Note FYI: Heat transfer between a reservoir and a system is an externally reversible process if the outer surface of the system is at the temperature of the reservoir.

As shown in Fig. 3.19 (c). Both processes are internally reversible, since both take place isothermally and both pass through exactly the same equilibrium states.

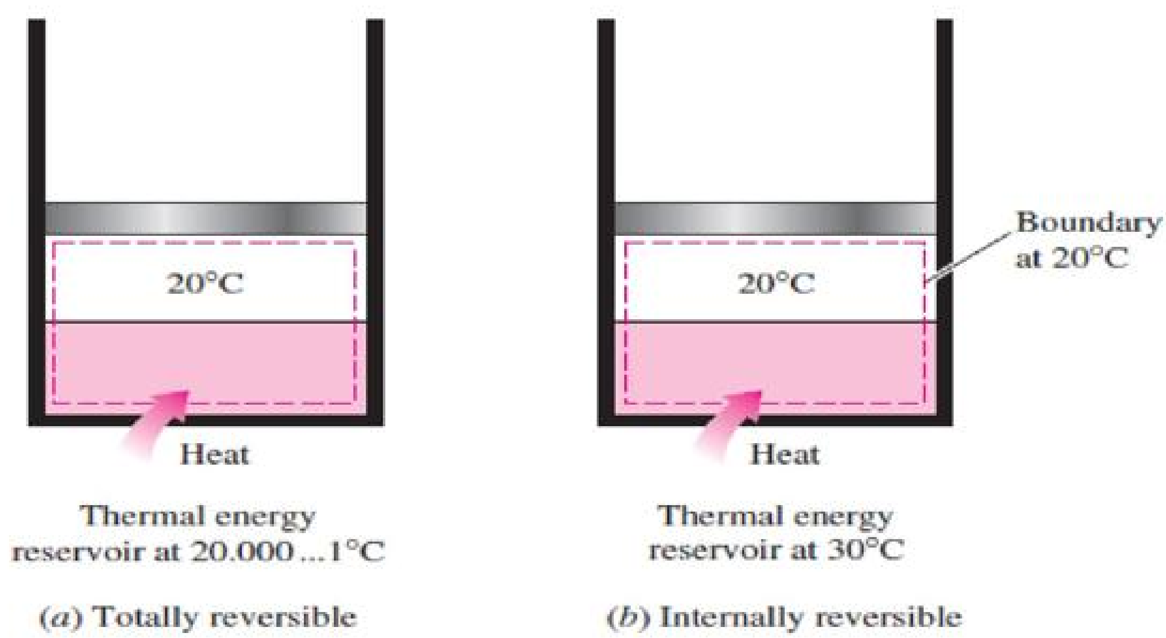


Fig. 3.19 (c) Totally and internally reversible heat transfer processes

– The first process shown is externally reversible also, since heat transfer for this process takes place through an infinitesimal temperature difference dT. The second process, however, is externally irreversible, since it involves heat transfer through a finite temperature difference dT.]

3. Mechanical Irreversibilities

These are associated with fluid friction (intermolecular friction) between the molecules and mechanical friction between the molecules and mechanical parts and friction between molecules and atmosphere.

4. Thermal Irreversibilities

These are associated with energy transfer as heat due to a finite temperature difference between parts of system or between system and its environment.

3.6 The Carnot Cycle (Carnot Heat engine)

Assumptions for Carnot cycle

1. The piston moving in a cylinder does not develop any friction during motion.
2. The walls of piston and cylinder are considered as perfect insulators of heat.
3. The cylinder head is so arranged that it can be a perfect heat conductor or perfect heat insulator.
4. The transfer of heat does not affect the temperature of source or sink.
5. Working medium is a perfect gas and has constant specific heat.
6. Compression and expansion are reversible.

The Carnot cycle is composed of four reversible processes—two isothermal and two adiabatic. Consider a closed system that consists of a gas contained in an adiabatic piston–cylinder device, as shown in Fig. 3.20 the insulation of the cylinder head is such that it may be removed to bring the cylinder into contact with reservoirs to provide heat transfer.

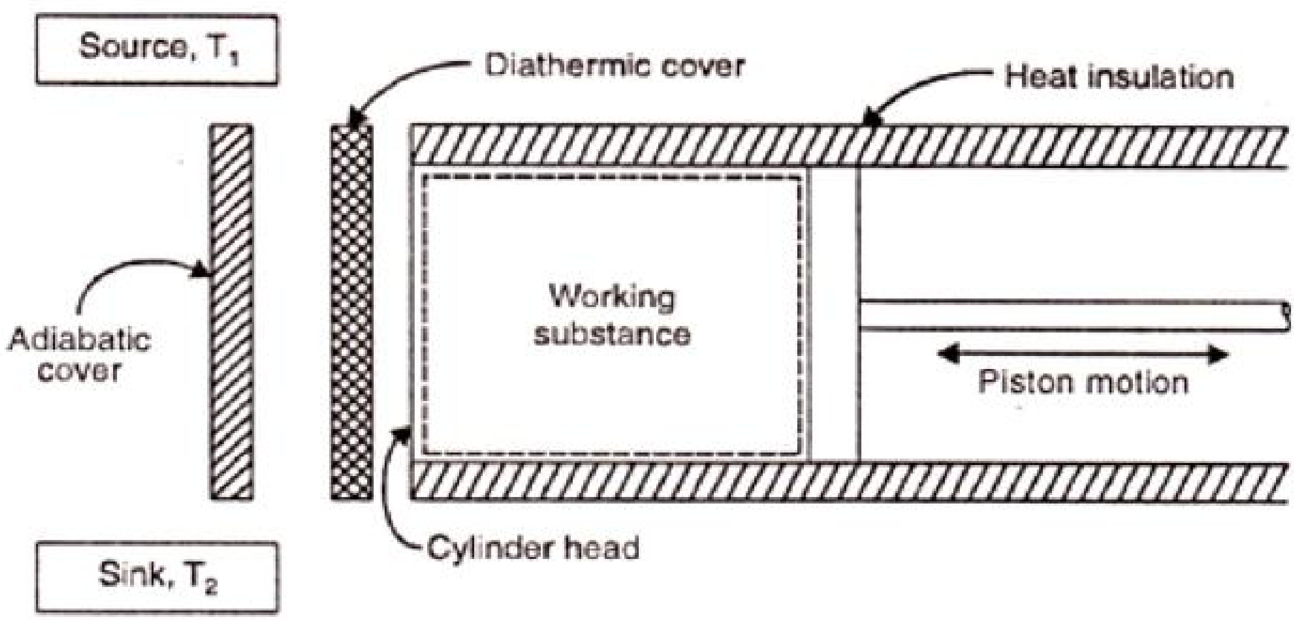


Fig. 3.20 Execution of the Carnot cycle in a closed system

– *Reversible Isothermal Expansion* (process 1-2, $T_H =$ constant): In this process, high temperature energy source is put contact with cylinder head by dithermic cover and Q_1 amount heat is supplied while the gas expands isothermally at temperature T_H. The amount of heat transferred to the gas during this process is given by,

$$Q_1 = W_{1-2} = P_1V_1 \ln\frac{V_2}{V_1} = mRT_H \ln\frac{V_2}{V_1}$$

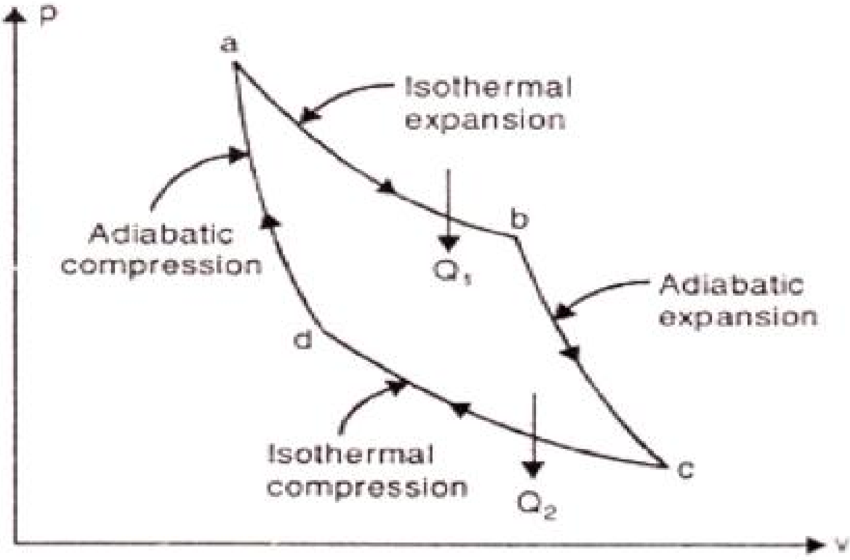


Fig. 3.21 P-v and T-s diagram of the Carnot cycle

– *Reversible Adiabatic Expansion* (process 2-3): In this process the adiabatic cover is put contact on the cylinder head, and the gas is expanded adiabatically, thus the temperature decreases from T_H to T_L.

– *Reversible Isothermal Compression* (process 3-4, $T_L =$constant): In this process, low temperature energy sink is put contact with cylinder head by dithermic cover and Q_2 amount of heat is rejected while the gas compressed isothermally at temperature T_L The amount of total heat transferred from the gas during this process is given by,

$$Q_2 = W_{3-4} = P_3V_3 \ln\frac{V_3}{V_4} = mRT_L \ln\frac{V_3}{V_4}$$

– Reversible *Adiabatic Compression* (process 4-1): In this process the adiabatic cover is put contact on the cylinder head, and the gas is compressed adiabatically, thus temperature increases from T_L to T_H and returns to its initial state 1 to complete the cycle.

Thermal efficiency of Carnot cycle is given by,

$$\eta_{th} = \frac{W_{net}}{Q_1}$$

As there is not heat interaction along the reversible adiabatic processes 2-3 and 4-1, and application of first law of thermodynamics for the complete cycle gives,

$$\delta W = \delta Q$$

$$W_{net} = Q_1 - Q_2 = mRT_H \ln\frac{V_2}{V_1} - mRT_L \ln\frac{V_3}{V_4}$$

Substituting the values of W_{net} in above equation we get,

$$\eta_{th,Carnot} = \frac{mRT_H \ln\frac{V_2}{V_1} - mRT_L \ln\frac{V_3}{V_4}}{mRT_H \ln\frac{V_2}{V_1}}$$

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H}\frac{\ln\frac{V_3}{V_4}}{\ln\frac{V_2}{V_1}}$$

For the adiabatic expansion and compression process 2-3 and 4-1,

$$\frac{T_2}{T_3} = \frac{T_H}{T_L} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \text{ and } \frac{T_1}{T_4} = \frac{T_H}{T_L} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\frac{T_H}{T_L} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\left(\frac{V_3}{V_2}\right) = \left(\frac{V_4}{V_1}\right) or \left(\frac{V_3}{V_4}\right) = \left(\frac{V_2}{V_1}\right)$$

Substitute the values in above equation, we get,

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H}$$

Conclusions from Carnot heat engine are:

1. The efficiency is independent of the working fluid and depends upon the temperature of source and sink. Being a reversible cycle, the Carnot cycle is the most efficient cycle operating between two specified temperature limits.
2. If $T_L = 0$, the engine will have an efficiency of 100%. However that means absence of heat sink which is violation of Kelvin-Plank statement of the second law.
3. The efficiency is directly proportional with the Temperature difference $T_H - T_L$ between the source and sink. Thermal efficiency increases with an increase in the average temperature at which heat is supplied to the system or with a decrease in the average temperature at which heat is rejected from the system. If $T_H = T_L$, no work will be done and efficiency will be zero.

- 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.

The Carnot cycle is impracticable because of the following reasons:

1. All the four processes have to be reversible. This necessitates that working fluid must have no internal friction between the fluid particle and no mechanical friction between the piston and cylinder wall. It is impossible to perform a frictionless process.

2. The heat absorption and rejection take place with infinitesimal temperature difference. Accordingly the rate of energy transfer will be very low and the engine will deliver only infinitesimal power. It is impossible to transfer the heat without temperature potential.
3. Isothermal process can be achieved only if the piston moves very slowly to allow heat transfer so that the temperature remains constant. Also Reversible isothermal heat transfer is very difficult to achieve in reality because it would require very large heat exchangers and it would take a very long time (a power cycle in a typical engine is completed in a fraction of a second). Therefore, it is not practical to build an engine that would operate on a cycle that closely approximates the Carnot cycle.

   Adiabatic process can be achieved only if the piston moves as fast as possible so that the heat transfer is negligible due to very short time available. The isothermal and adiabatic processes take place during the same stroke therefore the piston has to move very slowly for part of the stroke and it has to move very fast during remaining stroke. This variation of motion of the piston during the same stroke is not possible.
4. The source and sink temperatures that can be used in practice are not without limits, however. The highest temperature in the cycle is limited by the maximum temperature that the components of the heat engine, such as the piston or the turbine blades, can withstand. The lowest temperature is limited by the temperature of the cooling medium utilized in the cycle such as a lake, a river, or the atmospheric air.
5. There is insignificant difference in the slopes of isothermal and adiabatic lines. Consequently the p-v plot is greatly extended both in horizontal and vertical directions. The cylinder involves great pressure and volumes, and thus becomes bulky and heavy.

3.7 The Reversed Carnot Cycle (Carnot Refrigerator or Carnot heat pump)

- The Carnot heat-engine cycle just described is a totally reversible cycle. Therefore, all the processes that comprise it can be reversed, in which case it becomes the Carnot refrigeration cycle. Refrigerator and heat pump are *reversed heat engines*.
- This time, the cycle remains exactly the same, except that the directions of any heat and work interactions are reversed: Heat in the amount of Q_2 is absorbed from the low-temperature reservoir, heat in the amount of Q_1 is rejected to a high-temperature reservoir, and a work input of $W_{net,in}$ is required to accomplish all this. The P-V diagram of the reversed Carnot cycle is the same as the one given for the Carnot cycle, except that the directions of the processes are reversed, as shown in Fig. 3.22.

Process 1-2: Isentropic expansion of the working fluid in the clearance space of the cylinder. The temperature falls from T_H to T_L.

Process 2-3: Isothermal expansion during which heat Q_2 is absorbed at temperature T_L from the space being cooled.

Process 3-4: Isothermal compression of working fluid. The temperature rises from T_L to T_H.

Process 4-1: Adiabatic compression of working fluid during which heat Q_1 is rejected to a system at higher temperature.

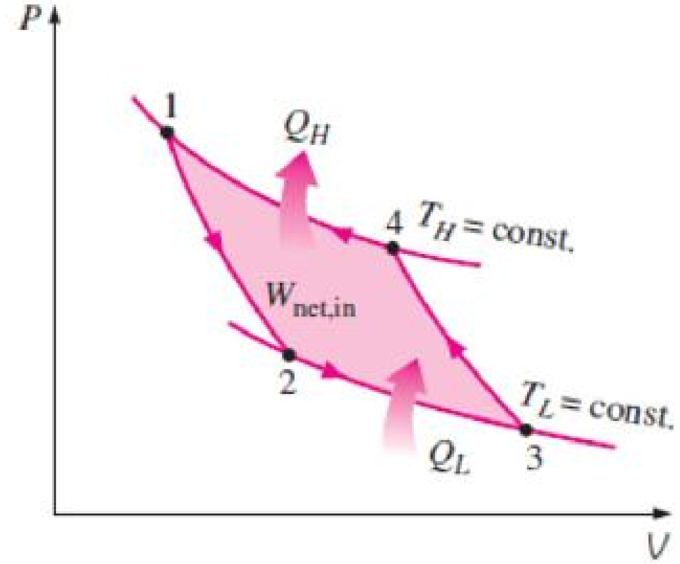


Fig. 3.22 P-V diagram of the reversed Carnot cycle

By using equations outlines in Carnot heat engine,

For Carnot heat pump,

$$COP_{HP} = \frac{Q_1}{Q_1 - Q_2} = \frac{mRT_H \ln \frac{V_2}{V_1}}{mRT_H \ln \frac{V_2}{V_1} - mRT_L \ln \frac{V_3}{V_4}}$$

$$\boxed{COP_{HP} = \frac{T_1}{T_1 - T_2}}$$

For Carnot refrigerator,

$$COP_R = \frac{Q_2}{Q_1 - Q_2} = \frac{mRT_L \ln \frac{V_2}{V_1}}{mRT_H \ln \frac{V_2}{V_1} - mRT_L \ln \frac{V_3}{V_4}}$$

$$\boxed{COP_R = \frac{T_2}{T_1 - T_2}}$$

3.8 The Carnot Theorem and Carnot Corollaries

3.8.1 Carnot Theorem and Its Proof

Carnot Theorem:

“The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.”

Thus if $\eta_{A(Rev)} > \eta_{B(Irev)}$; $W_A > W_B$; $Q - W_A < Q - W_B$ (according to Carnot theorem)

Proof of Carnot Theorem

- Consider a reversible engine E_A and an irreversible engine E_B operating between the same thermal reservoirs at temperatures T_1 and T_2 as shown in Fig. 3.23 (a). For the same quantity of heat Q withdrawn from the high temperature source, the work output from these engines is W_A and W_B respectively. As such the heat rejected is given by the reversible engine E_A is $Q - W_A$ and that from irreversible engine is $Q - W_B$.

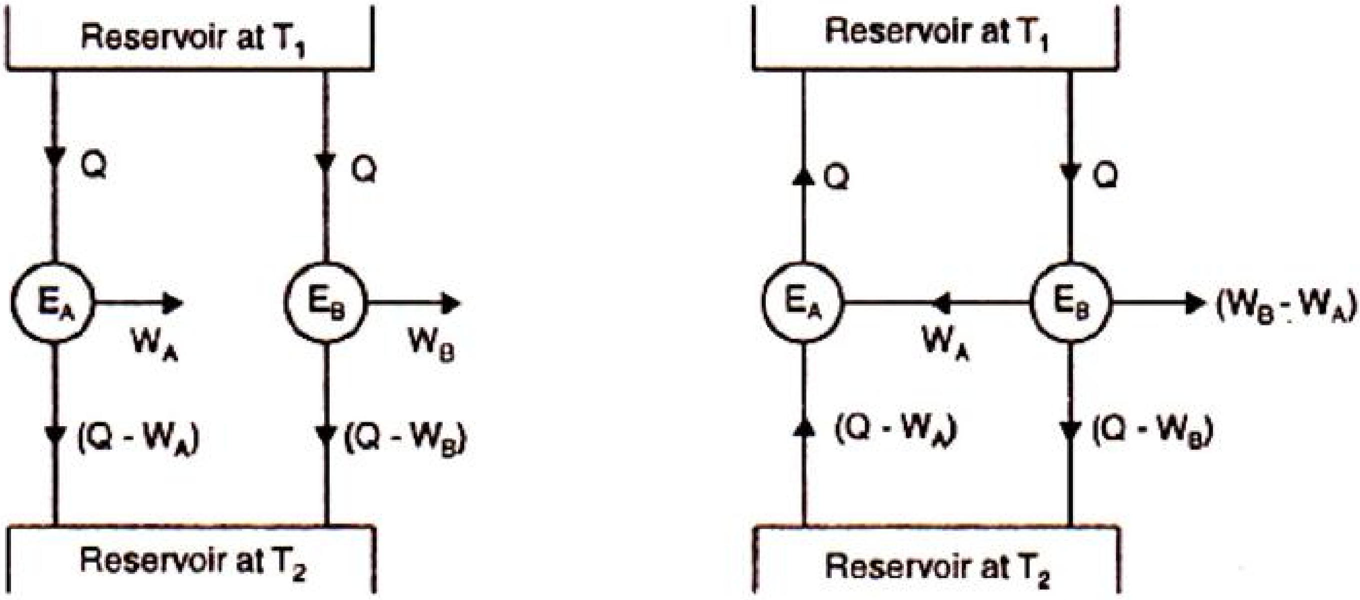


Fig. 3.23 (a) The proof of Carnot theorem

- Let us assume that $\eta_{B(Irev)} > \eta_{A(Rev)}$; $W_B > W_A$; $Q - W_B < Q - W_A$ (violation of Carnot theorem). Thus if irreversible engine E_B delivered $W_B - W_A$ more amount of work than the first reversible engine E_A and W_A is utilized to run reversible refrigerator R_A by reversing the reversible engine E_A then composite system as shown in Fig. 3.23 is an engine that produces a net amount of work while exchanging heat with a single reservoir which is the violation of Kelvin-Plank statement (PMM-2).
- Therefore, we conclude that no irreversible heat engine can be more efficient than a reversible one operating between the same two reservoirs, thus our assumption $\eta_{B(Irev)} > \eta_{A(Rev)}$ is wrong, because $\eta_{A(Rev)} > \eta_{B(Irev)}$ is only true to satisfy Carnot theorem.

3.8.2 Carnot Corollaries

Corollary-1

“All reversible heat engines operating between the two thermal reservoirs with fixed temperature have same efficiencies.”

Thus $\eta_{A(Rev)} = \eta_{B(Rev)}$; $W_A = W_B$; $Q - W_A = Q - W_B$ (according to Carnot corollary-1)

- Consider a reversible engine E_A and reversible engine E_B operating between the same thermal reservoirs at temperatures T_1 and T_2 as shown in Fig. 3.23 (b). For the same quantity of heat Q withdrawn from the high temperature source, the work output from these engines is W_A and W_B respectively. As such the heat rejected is given by the reversible engine E_A is $Q - W_A$ and that from reversible engine E_B is $Q - W_B$.

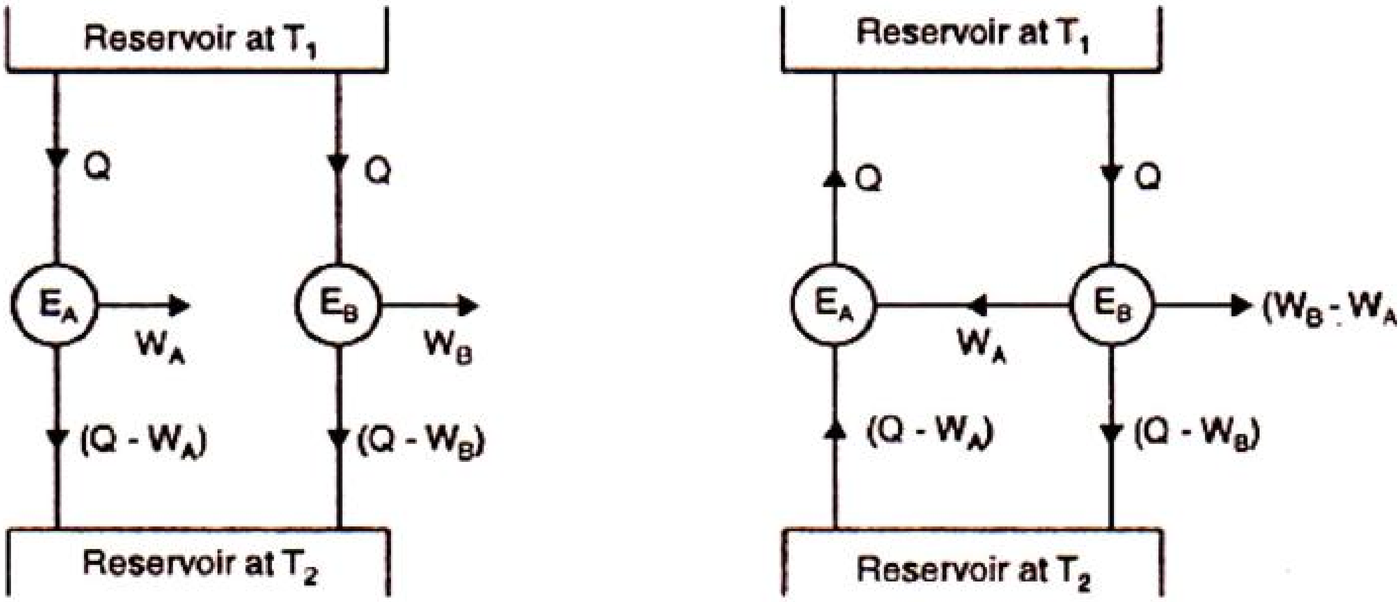


Fig. 3.23 (b) The proof of Carnot corollary-1

- Now let us assume that $\eta_{B(Rev)} > \eta_{A(Rev)}$; $W_B > W_A$; $Q - W_B < Q - W_A$ (violation of Carnot corollary-1). Thus reversible engine E_B delivered *(W_B -W_A)* more amount of work then the first reversible engine E_A and W_A is utilized to run reversible refrigerator R_A by reversing the reversible engine E_A then composite system as shown in Fig. 3.23 (b) is an engine that produces a net amount of work while exchanging heat with a single reservoir which is the violation of Kelvin-Plank statement (PMM-2).
- Therefore, we conclude that no any reversible heat engine can be more efficient than other reversible heat engine when operating between the same two thermal reservoirs, thus our assumption $\eta_{B(Rev)} > \eta_{A(Rev)}$ is wrong, because $\eta_{A(Rev)} = \eta_{B(Rev)}$ is only true to satisfy Carnot corollary-1.

Corollary-2

"The efficiency of any reversible heat engine operating between two thermal reservoirs is independent of the nature of working fluid and depends only on the temperature of thermal reservoirs."

3.9 Thermodynamic Temperature Scale

Definition: "A temperature scale that is independent of the properties of the thermometric substance that are used to measure temperature is called a thermodynamic temperature scale."

- A thermodynamic temperature scale is established based on fact that the thermal efficiency of reversible heat engines is a function of the reservoir temperatures only. That is,

$$\eta_{th,rev} = \phi(t_1, t_2)$$

Where ϕ signify the form of function that connects the temperature with temperature scale and it independent of the properties of the working fluid. The nature of ϕ need to be determine to give thermodynamic temperature scale.

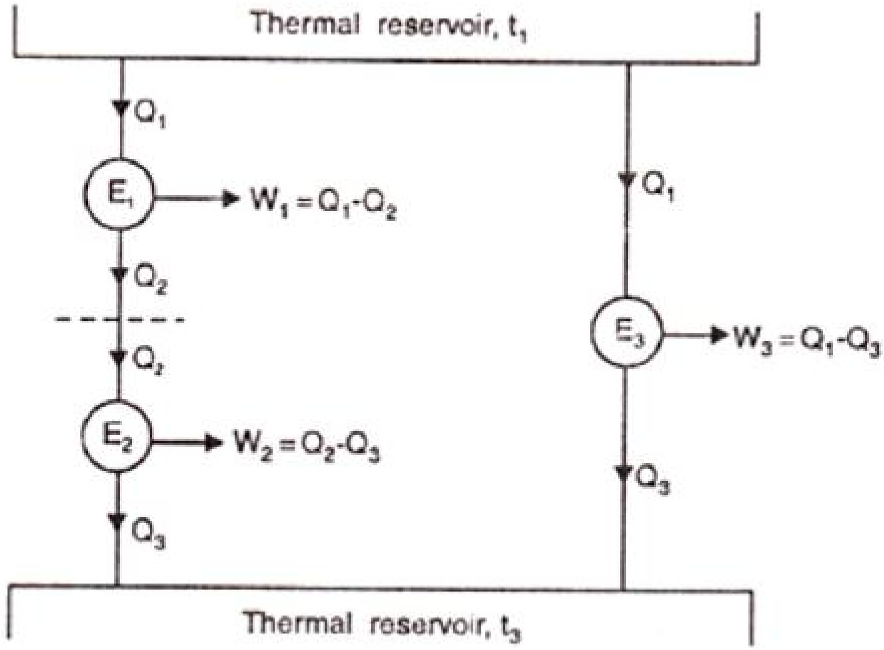


Fig. 3.24 Concept of thermodynamics temperature scale

- Consider two reversible engines E_1 is supplied with Q_1 amount of heat from the high temperature reservoir at t_1 and rejects Q_2 amount of heat at low temperature reservoir t_2 which is directly receives by reversible heat engine E_2 which further rejects Q_3 to the low temperature reservoir at t_3 as shown in Fig. 3.24.
- The amounts of heat rejected by engines E_1 and E_2 must be the same since engines E_1 and E_2 and can be combined into one reversible engine operating between the same reservoirs as engine E_3 and thus the combined engine will have the same efficiency as engine E_3. Thus we can write for each reversible engine,

$$\eta_{rev1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{1}{Q_1/Q_2} = 1 - \frac{1}{f(t_1, t_2)}$$

$$\eta_{rev2} = 1 - \frac{Q_2}{Q_3} = 1 - \frac{1}{Q_2/Q_3} = 1 - \frac{1}{f(t_2, t_3)}$$

Thus we can write for combine reversible engine,

$$\eta_{rev3} = 1 - \frac{Q_1}{Q_3} = 1 - \frac{1}{Q_1/Q_3} = 1 - \frac{1}{f(t_1, t_3)}$$

Thus we can write,

$$\frac{Q_1}{Q_2} = f(t_1, t_2); \frac{Q_2}{Q_3} = f(t_2, t_3); \frac{Q_1}{Q_3} = f(t_1, t_3)$$

Now consider the identity,

$$\frac{Q_1}{Q_2} = \frac{Q_1/Q_3}{Q_2/Q_3}; \; f(t_1, t_2) = \frac{f(t_1, t_3)}{f(t_2, t_3)}$$

- Above equation reveals that the left-hand side is a function of t_1 and t_2, and therefore the right-hand side must also be a function of t_1 and t_2 only. That is, the value of the product on the right-hand side of this equation is independent of the value of t_2. This condition will be satisfied only if the function f has the following form:

$$\frac{Q_1}{Q_2} = f(t_1, t_2) = \frac{\psi(t_1)}{\psi(t_2)}$$

Where ψ is another function of t. The choice of function ψ depends upon chosen scale of temperature and has infinite variety of forms. If the single form is selected it may written as,

$$\therefore \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

- This temperature scale is called the Kelvin scale, and the temperatures on this scale are called absolute temperatures. On the Kelvin scale, the temperature ratios depend on the ratios of heat transfer between a reversible heat engine and the reservoirs and are independent of the physical properties of any substance.

3.10 Solved Numerical

Example 3.1 An engine manufacturer claims to have developed a heat engine with following specifications:

Power developed	= 75 kW
Fuel burnt	= 5 kg/hr
Heating value of fuel	= 75000 kJ/kg
Temperature limits	= 1000 K and 400 K

Is the claim of an engine manufacturer true or false? Provide your explanation.

Solution:

Given data:

$P = 75\ \text{kW}$

$m_f = 5\ \text{kg/hr}$

$C.V = 75000\ \text{kJ/kg}$

$T_1 = 1000\ \text{K}, T_2 = 400\ \text{K}$

Find:

Check the claim

Work done = 75 kW = 75 x 3600 = 27 X 10^4 kJ/hr

Heat supplied = $m_f \times C.V = 5 \times 75000 = 37.5 \times 10^4 \text{kJ/hr}$

For given heat engine, thermal efficency is,

$$\eta_{th} = \frac{\text{Workdone}}{\text{heat supplied}} = \frac{27 \times 10^4}{37.5 \times 10^4} = 72\%$$

But thermal efficiency of reversible heat engine,

$$\eta_{th} = \frac{T_1 - T_2}{T_1} = \frac{1000 - 400}{1000} = 0.6 = 60\%$$

Since manufacturere claim is falsed because its efficiency is greater than reversible efficiency.

Example 3.2 A heat engine is supplied with 2512 kJ/min of heat at 650°C. Heat rejection takes place at 100°C. Specify which of the following heat rejections represents reversible, irreversible and impossible results: (i) 867 kJ/min, (ii) 1015 kJ/min, (iii) 1494 kJ/min.

Solution:

Given data:

$T_1 = 650^0\text{C} = 650 + 273 = 923\ \text{K}$

$T_2 = 100^0\text{C} + 273 = 373\ \text{K}$

Find:

Specify the type of heat engine

$$(i)\oint\frac{\delta Q}{T}=\frac{Q_1}{T_1}-\frac{Q_2}{T_2}=\frac{2512}{923}+\frac{867}{373}=0.347>0$$

This cycle is impossible

$$(ii)\oint\frac{\delta Q}{T}=\frac{Q_1}{T_1}-\frac{Q_2}{T_2}=\frac{2512}{927}-\frac{1015}{373}=0$$

This cycle is revesrible.

$$(iii)\oint\frac{\delta Q}{T}=\frac{Q_1}{T_1}-\frac{Q_2}{T_2}=\frac{2512}{927}+\frac{1494}{373}=-1.284<0$$

This cycle is irrevesrible.

Example 3.3 A reversible engine receives heat from two thermal reservoirs maintained at constant temperature of 750 K and 500 K. The engine develops 100 kW and rejects 3600 kJ/min of heat to a heat sink at 250 K. Determine thermal efficiency of the engine and heat supplied by each thermal reservoir.

Solution:

Given data:

$T_1 = 750$ K

$T_2 = 500$ K

$T_3 = 250$ K

$W = 100$ kW $= 6000$ kJ / min

Heat rejected $= 3600$ kJ/min

Find:

(1) η_{th}

(2) heat supplied by source at 750 K

& heat supplied by source at 500 K

Application of first law of thermodynamics to heat engine gives,

Total heat supplied = 6000 + 3600 = 9600 kJ/min

$$\text{Efficiency} = \frac{\text{Work done}}{\text{heat supllied}}=\frac{6000}{9600}=0.625=62.5\%$$

Let Q is the heat supplied by source A. then heat supplied by source B is (9600 - Q).

As the heat engine is reversible, the Clausius theorem gives

$$\oint\frac{\delta Q}{T}=0=\frac{Q}{750}+\frac{9600-Q}{500}+\frac{3600}{250}$$

$$Q=7200 \text{ kJ/min}$$

Thus heat supplied by source at 750 K = 7200 kJ/min

and heat supplied by source at 500 K = $(9600-7200)=2400$ kJ/min

Example 3.4 Two reversible engines A and B are arranged in series. Engine 'A' rejects heat directly to engine 'B'. Engine 'A' receives 200 kJ at temperature of 421^{o}C from the hot source while engine 'B' is in communication with a cold sink at a temperature of 5^{o}C. If the work output of 'A' is twice that of 'B'. Find (1) intermediate temperature between A and B; (2) efficiency of each engine and (3) heat rejected to the sink.

Solution:

Given data:

$T_1 = 421^0C$

$T_3 = 5^0C$

$Q_1 = 200$ kJ

$W_A = 2W_B$

Find:

(1) T_2

(2) η_{th_A} and η_{th_B}

(3) Q_2 and Q_3

Work delivered by engines A and B are,

$$W_1 = Q_1 - Q_2 \text{ and } W_2 = Q_2 - Q_3$$

Since each engine delevers the same amount of work

$$Q_1 - Q_2 = (Q_2 - Q_3)$$

$$Q_1 + 2Q_3 = 3Q_2$$

$$\frac{Q_1}{Q_2} + 2\frac{Q_3}{Q_2} = 3 \text{....(i)}$$

Further the engines are revrsible, therefore

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \text{ and } \frac{Q_2}{Q_3} = \frac{T_2}{T_3} \text{...(ii)}$$

Substitute values of eq (ii) in eq (i),

$$\frac{T_1}{T_2} + 2\frac{T_3}{T_2} = 3$$

$$\frac{694}{T_2} + 2 \times \frac{278}{T_2} = 3$$

$$T_2 = 416.67 \text{ K}$$

Efficiency of engine A,

$$\eta_A = \frac{T_1 - T_2}{T_1} = \frac{694 - 416.67}{416.67} = 0.3996 \text{ or } 39.96\%$$

Efficiency of engine B,

$$\eta_B = \frac{T_2 - T_3}{T_2} = \frac{416.67 - 218}{416.67} = 0.3328 \text{ or } 33.28\%$$

From eq (ii)

$$Q_2 = Q_1 \times \frac{T_1}{T_2} = 200 \times \frac{416.67}{694} = 120.08 \text{ kJ}$$

$$Q_3 = Q_2 \times \frac{T_3}{T_2} = 120.08 \times \frac{278}{416.67} = 80.12 \text{ kJ}$$