3

Second Law of Thermodynamics

Contents

3.1 Introduction

- First law of thermodynamics deals with conservation and conversion of energy. It stipulates that when a thermodynamic process is carried out, energy is neither gained nor lost. Energy only transforms from one form into another and the energy balance is maintained. The law, however, fails to state the condition under which energy conversions are possible. The law presumes that any change of a thermodynamic state can take place in either direction.
- However, this is not true; particularly in the inter-conversion of heat and work. Processes proceed spontaneously in certain directions but not in opposite directions, even though the reversal of processes does not violate the first law.

3.2 Examples of First law

- It is common experience that a cup of hot coffee left in a cooler room eventually cools off. 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.

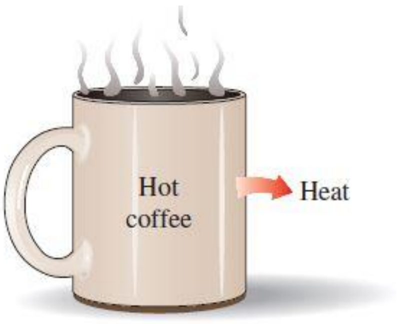

Fig.3.1 - A cup of hot coffee does not get hotter in a cooler room

- As another familiar example, consider the heating of a room by the passage of electric current through a resistor. Again, the first law says 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.

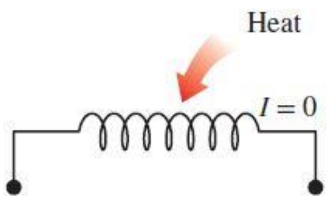

Fig.3.2 - Transferring heat to a wire will not generate electricity

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

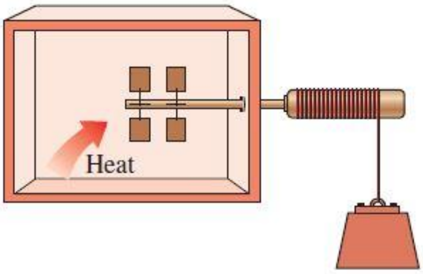

Fig.3.3 - Transferring heat to a paddle wheel will not cause it to rotate

- 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.
- 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.
- 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.
- Fuels (coals, diesel, and petrol) burns with air to form the products of combustion. Fuels once burnt cannot be restored back to original from.
- 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.3.4 - 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.

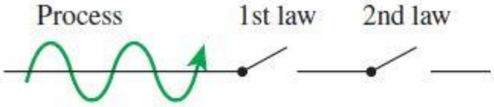

Fig.3.5 - A process must satisfy both the first and second laws of thermodynamics to proceed

- 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

- First law does not help to predict whether the certain process is possible or not.
- A spontaneous process can proceed in a particular direction only, but first law does not give information about direction.
- First law not provides sufficient condition for a certain process to take place.
- First law establishes equivalence between the amount of heat used and mechanical work, but does not specify the conditions under which conversion of heat into work is possible, neither the direction in which heat transfer can take place.

3.3 Basic Definitions

3.3.1 Thermal Energy Reservoir

- It is defined as sufficiently large system in stable equilibrium that can supply or absorb finite amount of heat without any change in its temperature.
- A thermal reservoir is thus characterized by its temperature which remains constant.
- In practice, large bodies of water such as oceans, lakes, rivers, and atmospheric air can be considered thermal energy reservoirs.

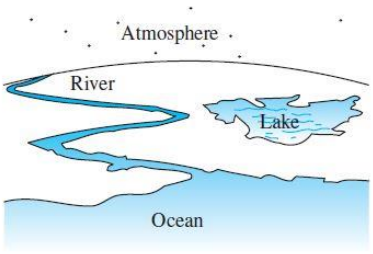

Fig.3.6 - Thermal energy reservoirs

3.3.2 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.

3.3.3 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.

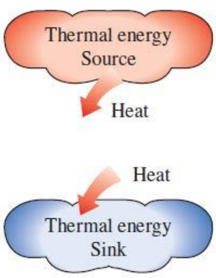

Fig.3.7 - Heat source and Heat sink

3.3.4 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:
    - It receives heat from a high-temperature source at temperature T_1 (furnace, nuclear reactor, solar energy etc.)
    - It converts the part of this heat to work (mostly in the form of a rotating shaft).
    - It rejects the remaining waste heat to a low-temperature sink (the atmosphere, rivers etc.).
    - It operates on complete thermodynamic cycle.

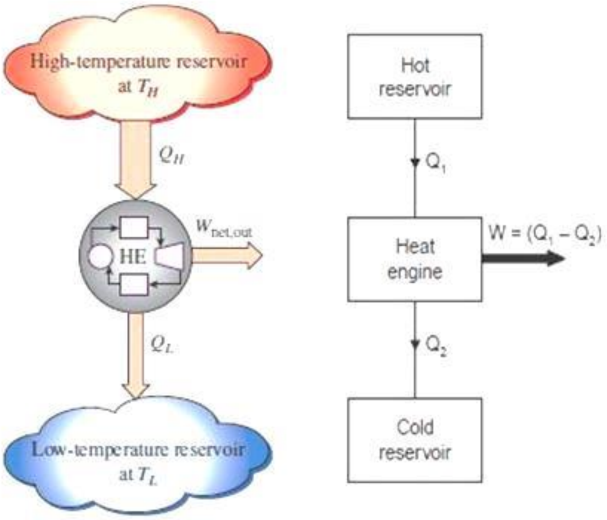

Fig.3.8 - Heat engine

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,

$$\eta = \frac{Desired\ work\ output}{Required\ Heat\ input} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_2}{Q_1} \qquad \textit{Eq. (3.1)}$$

Where Q_1= Heat supplied to system, kJ

Q_2= Heat rejected from system, kJ

W= Net work done by a system, kJ

3.3.5 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.
- The objective of a refrigerator is to maintain the refrigerated space at a low temperature by absorbing heat from it and reject to higher-temperature medium.

Coefficient of Performance of Refrigerator

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

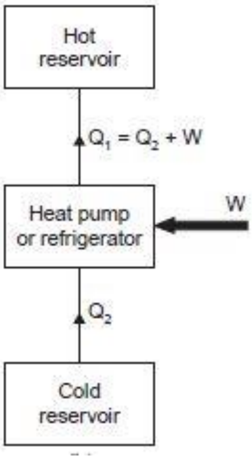

Fig.3.9 – Heat pump or Refrigerator

- Mathematically,

$$COP_{REf} = \frac{Desired\ work\ output}{Work\ required\ in\ compressor} = \frac{Q_2}{W_{in}} = \frac{Q_2}{Q_1 - Q_2} \qquad \textit{Eq. (3.2)}$$

3.3.6 Heat Pump

- It is defined as the mechanical device that transfers heat from a low-temperature medium to a high-temperature 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 and reject to higher temperature source.

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,

$$COP_{HP} = \frac{Desired\ work\ output}{Work\ required\ in\ compressor} = \frac{Q_1}{W_{in}} = \frac{Q_1}{Q_1 - Q_2} \qquad \textit{Eq. (3.3)}$$

3.3.7 Perpetual-Motion Machines (PMM)

- It is defined as the device that violates either law (first or second) is called a perpetual-motion machine.
- **PMM1:** A device that violates the first law of thermodynamics 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).

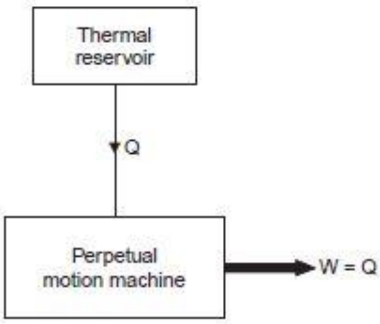

Fig.3.10 - Perpetual motion machine of second kind (PMM2)

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.

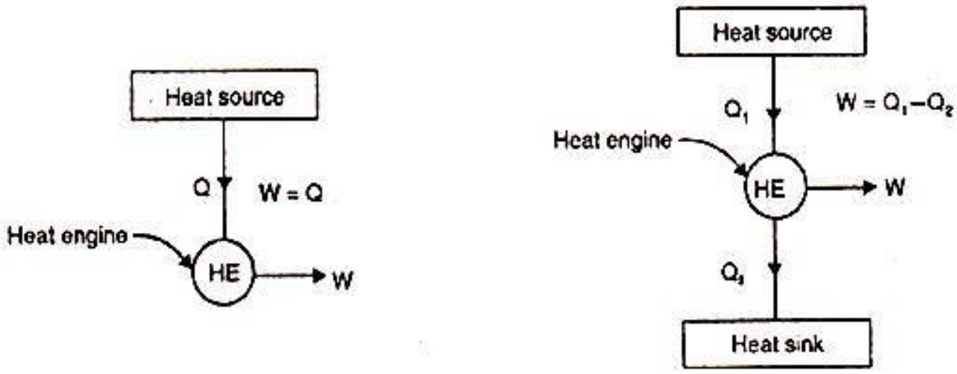

Fig.3.11 – (a) Impossible (b) Possible
Schematic representation of heat engine accordance with Kelvin–Planck statement

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.

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.

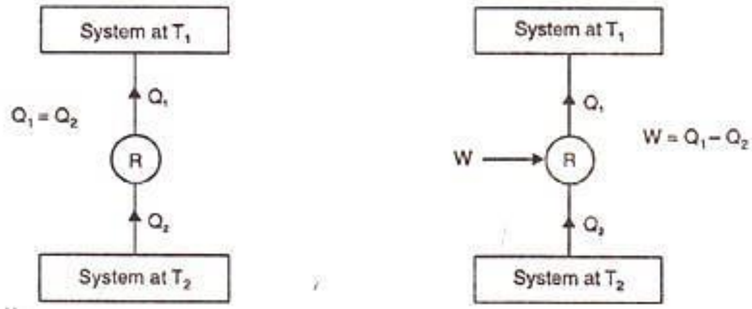

Fig.3.12 - (a) Impossible (b) Possible
Schematic representation of refrigerator accordance with the Clausius statement

3.4.3 Equivalency of the Two Statements

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

- As shown in Fig. (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. 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.

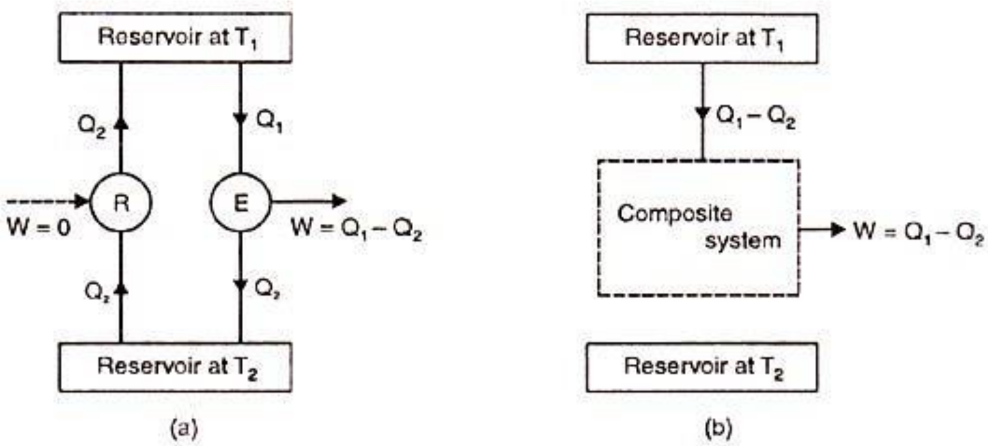

Fig.3.13 - Violation of the Clausius statement leads to the violation of the Kelvin–Planck statement

- As shown in Fig. (b) the 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 is violation of the Kelvin-Planck statement.

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

- As shown in Fig. (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 violation of the Kelvin-Planck statement.

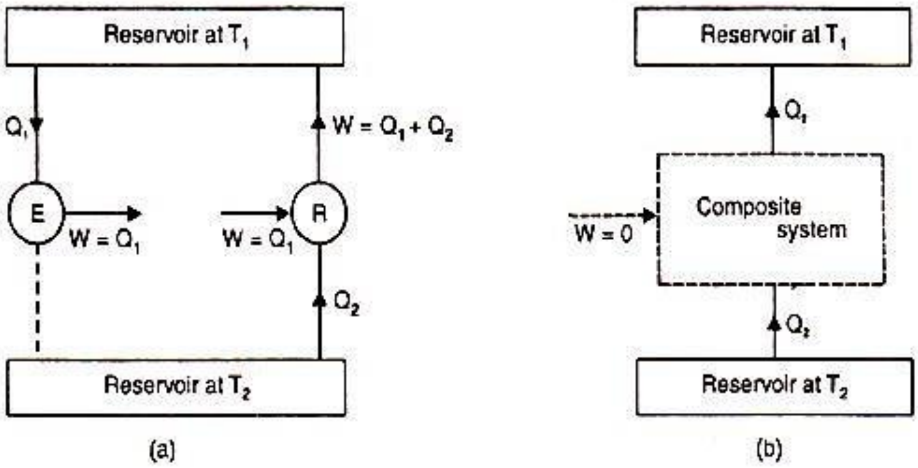

Fig.3.14 - Violation of the Kelvin–Planck statement leads to the violation of the Clausius statement

- 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.
- As shown in Fig. (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. This is in violation of the Clausius statement. Thus violation of Kelvin-Planck statement leads to violation of Clausius statement also.

3.5 The Carnot Theorem and Carnot Corollaries

3.5.1 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.

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 abd T_2 as shown in Fig. For the same quantity of heat Q withdrawn from the high temperature source, the work output from these engines is W_A & W_B respectively. As such the heat rejected is given by the reversible engine EA is Q-W_A and that from irreversible engine is Q-W_B.

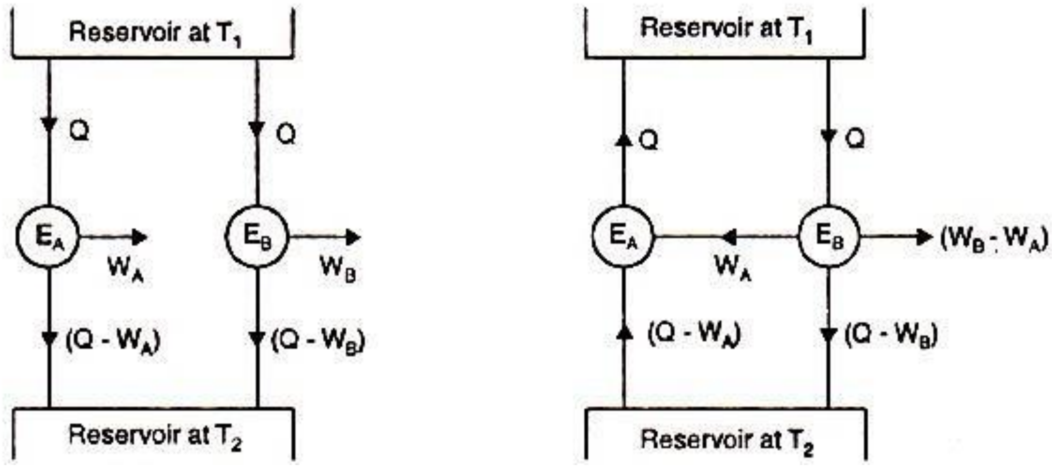

Fig.3.15 - Carnot theorem

- Let us assume that $\eta_{B(rev)} \geq \eta_{A(rev)}$, $W_B > W_A$, 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. 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 $\eta_{B(rev)} \geq \eta_{A(rev)}$ is wrong, because $\eta_{A(rev)} \geq \eta_{B(rev)}$ is only true to satisfy Carnot theorem.

3.5.2 Corollary-1

- All reversible heat engines operating between the two thermal reservoirs with fixed temperature have same efficiencies.
- Thus, $\eta_{B(rev)} = \eta_{A(rev)}$
- 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. For the same quantity of heat Q withdrawn from the high temperature source, the work output from these engines is W_A & 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.

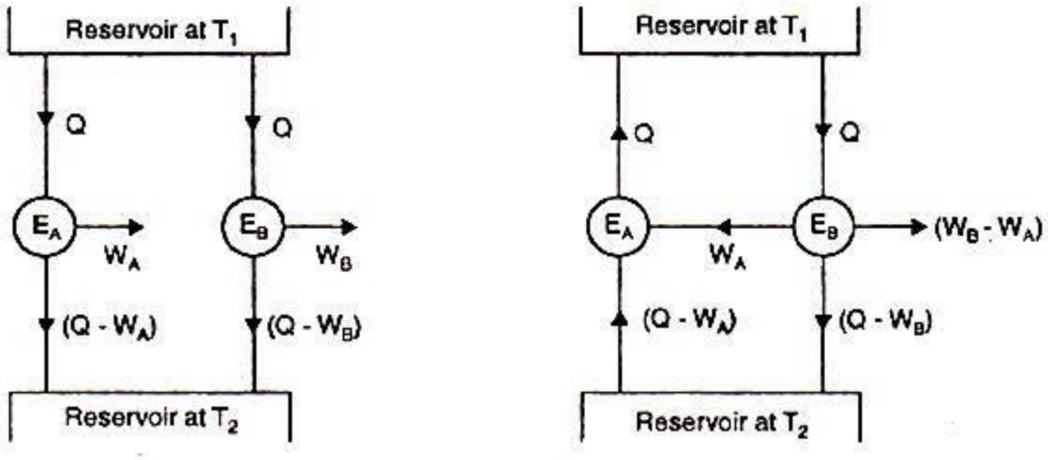

Fig.3.16 - Carnot corollary-1

- 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. 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, So, $\eta_{B(rev)} = \eta_{A(rev)}$ is only true to satisfy Carnot corollary-1.

3.5.3 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.
- As shown in *Fig.3.17 - Carnot corollary-2*. The efficiency is same because both are reversible engines and work on the Carnot cycle. Efficiency depends only upon the temperature of the reservoirs. So, work is produced by engine E equal to work is required to heat pump R.
- Now assumed that, efficiency of engine E be increased by changing nature of working substance. It is as shown in fig. means that the engine E produces more work and rejects less heat to sink.
- However engine E receives Q amount of heat from source and pump R delivers same amount of heat to source. Therefore, we can eliminate high temperature source and combined system as shown in Fig. receives W_E - W_R amount of heat from sink and produced same amount of work.
- This violates second law of the thermodynamics. Therefore it is concluded that efficiency does not depend on any properties of working fluid other than temperature of reservoirs.

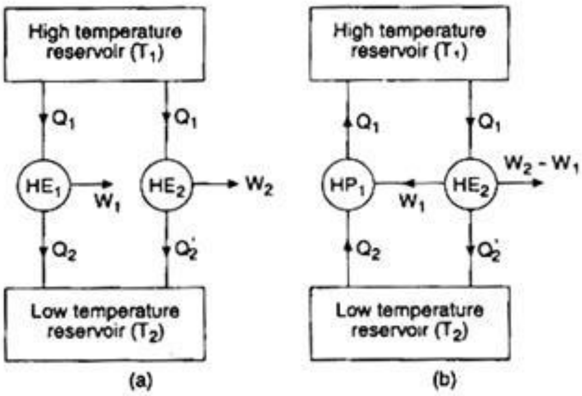

Fig.3.17 - Carnot corollary-2

3.6 Reversible and Irreversible Process

3.6.1 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

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

Salient Features

- 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.
- 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.
- 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.

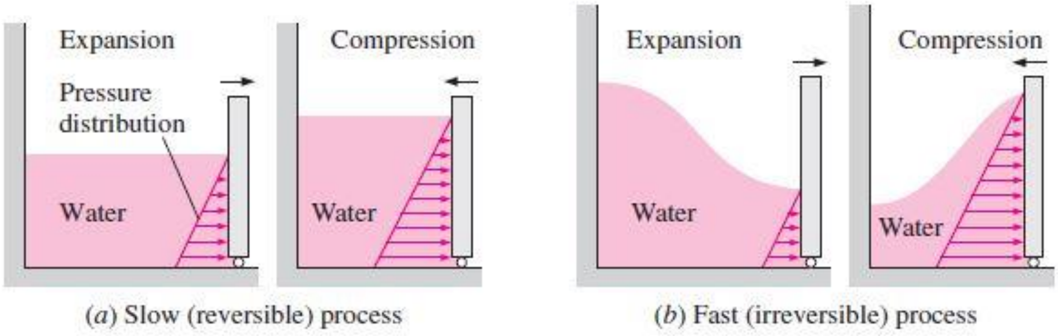

Fig.3.18 – Reversible and irreversible process

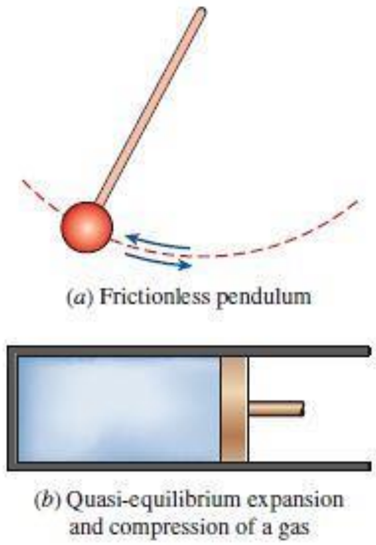

Fig.3.19 – Reversible processes

- Reversible processes can be viewed as theoretical limits for the corresponding irreversible ones.
- 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.
- 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.
- It is idealized process actually do not occur in nature.
- There should be no free or unrestricted expansion and no mixing of the fluids.

Some Notable Examples of ideal reversible processes are

- Motion without friction.
- Frictionless adiabatic and isothermal expansion or compression.
- Restricted and controlled expansion or compression.
- Elastic stretching of a solid.
- Restrained discharge of the battery.
- Electric circuit with zero resistance.
- Polarisation, magnetisation effects and electrolysis.
- Condensation and boiling of liquids.

3.6.2 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

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

Some Notable Examples of an irreversible process are

- Spontaneous chemical reaction.
- Viscous flow, fluid flow with friction.
- Inelastic deformation and hysteresis effects.
- Electric circuit with resistance.
- Diffusion of gases, mixing of dissimilar gases.
- Heat transfer takes place with finite temperature difference.
- Free expansion and throttling process.
- Friction sliding friction as well as friction in the flow of fluids

3.6.3 Irreversibilities

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

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.3.20 - Friction renders a process irreversible*. 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.
- 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.

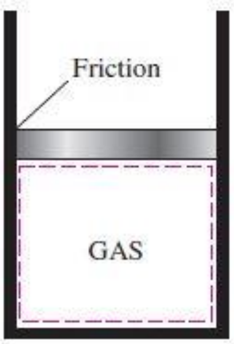

Fig.3.20 - Friction renders a process irreversible

2. Unrestrained expansion

- Unrestrained expansion of a gas separated from a vacuum by a membrane, as shown in *Fig.3.21 - Unrestrained expansion of a gas makes the process Irreversible* . 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.

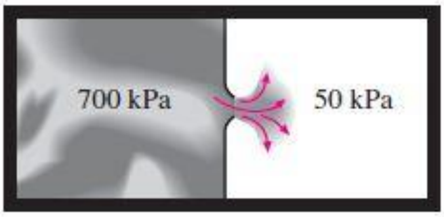

Fig.3.21 - Unrestrained expansion of a gas makes the process Irreversible

- 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

- Consider a can of cold soda left in a warm room as shown in *Fig.3.22 - (a) Heat transfer through temperature difference is irreversible, (b) the reverse process is impossible.* 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.

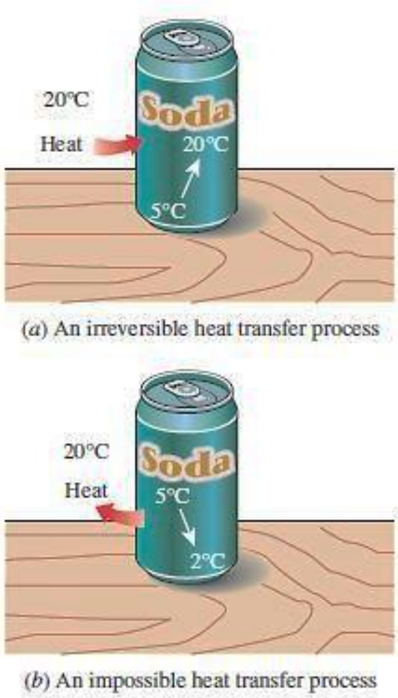

Fig.3.22 **-** *(a) Heat transfer through temperature difference is irreversible, (b) the reverse process is impossible.*

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.

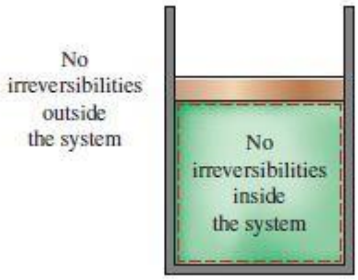

Fig.3.23 **-** *A reversible process involves no internal and external irreversibilities.*

- As shown in *Fig.3.25* **-** *The arrangement of heat engines used to develop the thermodynamic temperature scale.* Both processes are internally reversible, since both take place isothermally and both pass through exactly the same equilibrium states.
- 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.

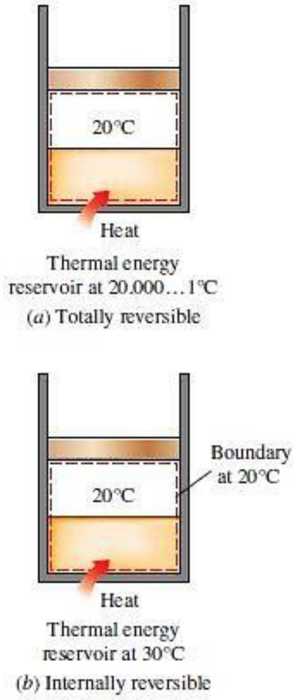

Fig.3.24 - Totally and internally reversible heat transfer processes.

3.7 Thermodynamic Temperature Scale

- A temperature scale that is independent of the properties of the substances 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.

$$\eta_{Rev} = \emptyset(T_1, T_2) \qquad \text{Eq. (3.4)}$$

- 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.
- 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.3.25 - The arrangement of heat engines used to develop the thermodynamic temperature scale.*
- 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,

$$\eta_{Rev1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{1}{\frac{Q_1}{Q_2}} = 1 - \frac{1}{f(T_1, T_2)} \qquad \text{Eq. (3.5)}$$

$$\eta_{Rev2} = 1 - \frac{Q_3}{Q_2} = 1 - \frac{1}{\frac{Q_2}{Q_3}} = 1 - \frac{1}{f(T_2, T_3)} \qquad \text{Eq. (3.6)}$$

- Thus we can write for combine reversible engine,

$$\eta_{Rev2} = 1 - \frac{Q_3}{Q_1} = 1 - \frac{1}{\frac{Q_1}{Q_3}} = 1 - \frac{1}{f(T_1, T_3)} \qquad \textit{Eq. (3.7)}$$

$$\frac{Q_1}{Q_2} = f(T_1, T_2) \qquad \textit{Eq. (3.8)}$$

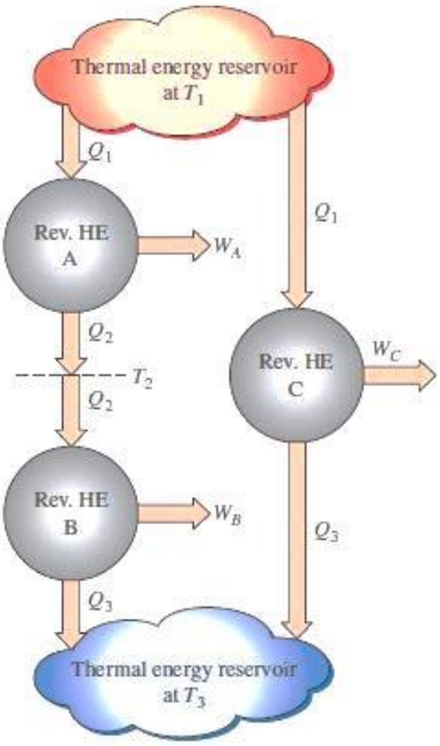

Fig.3.25 - The arrangement of heat engines used to develop the thermodynamic temperature scale.

- Applying Eq. 3.8 to all three engines separately, we obtain

$$\frac{Q_1}{Q_2} = f(T_1, T_2), \frac{Q_2}{Q_3} = f(T_2, T_3) \text{ and } \frac{Q_1}{Q_3} = f(T_1, T_3) \qquad \textit{Eq. (3.9)}$$

- Now consider the identity

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2}\frac{Q_2}{Q_3} \qquad \textit{Eq. (3.10)}$$

- Which corresponds to

$$f(T_1, T_3) = f(T_1, T_2) f(T_2, T_3) \qquad \textit{Eq. (3.11)}$$

- A careful examination of this equation reveals that the left-hand side is a function of T_1 and T_3, and therefore the right-hand side must also be a function of T_1 and T_3 only, and not T_2. 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:

$$f(T_1, T_2) = \frac{\varphi(T_1)}{\varphi(T_2)}, f(T_2, T_3) = \frac{\varphi(T_2)}{\varphi(T_3)} \text{ and } f(T_1, T_3) = \frac{\varphi(T_1)}{\varphi(T_3)} \qquad \textit{Eq. (3.12)}$$

- For a reversible heat engine operating between two reservoirs at temperatures T_H and T_L, can be written as

$$\frac{Q_H}{Q_L} = \frac{\varphi(T_H)}{\varphi(T_L)} \qquad \textit{Eq. (3.13)}$$

3.8 Reference Books:

1) Thermal Science and Engineering by D. S. Kumar
2) Fundamental of Engineering Thermodynamics by Michael J. Moran
3) Engineering Thermodynamics by R. K. Rajput
4) Engineering Thermodynamics by P. K. Nag
5) Thermodynamics an Engineering approach by Yunus A. Cengel