Reversibility, Irreversibility and Carnot cycle

The second law of thermodynamics distinguishes between reversible and irreversible processes.

- If a process can proceed in either direction without violating the second law of thermodynamics, it is reversible process. A reversible process is carried out infinitely slowly with an infinitesimal gradient, so that every state passed through by the system is an equilibrium state. So, a reversible process is a quasi-static process which can proceed in either direction.
- Given a process, if the attempt to reverse its direction leads to a violation of the second law of thermodynamics, then the given process is irreversible.

Any natural process carried out with a finite gradient is an **irreversible process** . A reversible process which consists of a succession of equilibrium states, is an idealized hypothetical process, approached only as a limit. **It is said to be an asymptote to reality**, All spontaneous processes are irreversible.

Irreversible Processes

The example of irreversible processes are: Motion with friction, free expansion, Expansion/ compression with finite pressure difference, Energy transfer as heat with finite ΔT, Mixing of matter at different states, Mixing of non-identical gases.

Reversible Processes

The processes which can be idealized as reversible are: Motion without friction, Expansion/compression with infinitesimal pressure difference, Energy transfer as heat with infinitesimal temperature difference.

Carnot Cycle

A French engineer Sadi Carnot was the first to introduce the idea of reversible cycle. From the second law, it has been observed that the efficiency of a heat engine is less than unity. If the efficiency of heat engine is less than unity, what is the maximum efficiency of a heat engine? This can be answered by considering the Carnot cycle. The concept of carnot cycle is executed via Carnot engine.

Carnot Engine

Let us consider the operation of a hypothetical engine which employs the Carnot cycle. The Carnot engine consists of a **cylinder-piston assembly** in which a certain amount of gas(working fluid) is enclosed. Refer to Figure 18.1 representing the Carnot cycle.

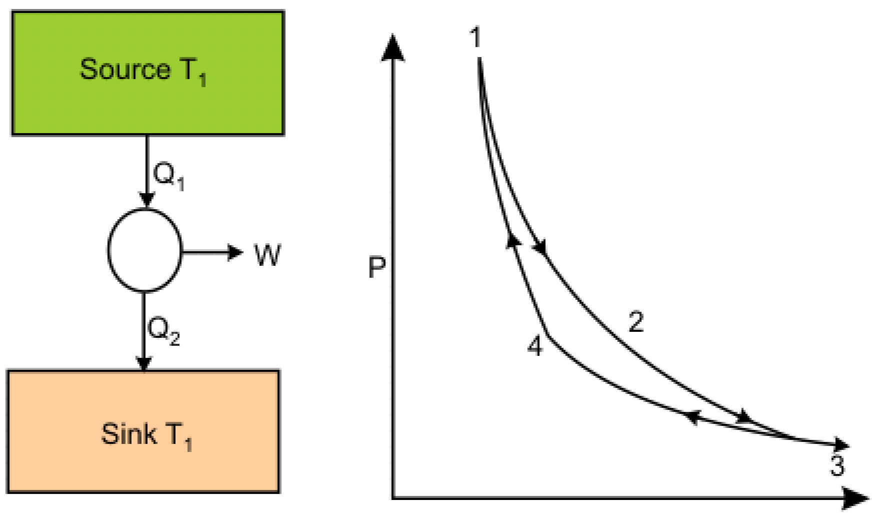

Figure 18.1

Reversible Isothermal Heat Addition

In the first process, the cylinder head is brought into contact with a source at temperature T_1. The gas inside the cylinder is also at temperature T_1. The gas expands **reversibly and isothermally.** During this process, the system absorbs energy as heat (Q_1) from the source. The system changes its state from 1 to 2 on the $P-v$ diagram.

$$Q_1 = (U_2 - U_1) + W_{1-2} \tag{18.1}$$

Where, for an ideal gas, $U_2 - U_1$

Reversible Adiabatic Expansion

In the second process, the cylinder head is insulated and the gas is allowed to expand till its temperature is equal to the sink temperature T_2. The system thus reaches state 3. **This is a reversible adiabatic process.**

$$0 = (U_3 - U_2) + W_{2-3} \quad (18.2)$$

Reversible Isothermal Heat Rejection

In the next process, the system is brought into contact with the sink which is at a temperature T_2. The heat Q_2 leaves the system and the internal energy further decreases

$$-Q_2 = (U_4 - U_3) - W_{3-4} \quad (18.3)$$

Where, only for an ideal gas, $U_4 = U_3$

Through a reversible isothermal process the system reaches state 4.

Reversible Adiabatic Compression

In the next process, the gas is compressed reversibly and adiabatically till it reaches the initial state 1, thus, completing the cycle.

$$0 = U_1 - U_4 - W_{4-1} \quad (18.4)$$

Summing up all the processes, one can write

$$Q_1 - Q_2 = (W_{1-2} + W_{2-3}) - (W_{3-4} + W_{4-1})$$

or,

$$\sum_{cycle} Q_{net} = \sum_{cycle} W_{net}$$

The thermal efficiency,

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \qquad (18.5)$$

Efficiency of Carnot Engine Using Ideal Gas

1-2: A reversible isothermal expansion with heat addition

$$Q_1 = \int_1^2 Pdv = RT_1 \ ln\left(\frac{v_2}{v_1}\right) \qquad (18.6)$$

2-3: A reversible adiabatic expansion

$$W = c_v\left(T_1 - T_2\right) \qquad (18.7)$$

3-4: A reversible isothermal compression with heat rejection

$$Q_2 = \int_3^4 Pdv = RT_2 \ ln\left(\frac{v_4}{v_3}\right) \qquad (18.8)$$

4-1: A reversible adiabatic compression

$$W = \int_4^1 du = c_v\left(T_2 = -T_1\right) \qquad (18.9)$$

$$\sum W = RT_1 \; In\left(\frac{\hat{v}_2}{\hat{v}_1}\right) + c_v\left(T_1 - T_2\right) + RT_2 \; In\left(\frac{v_4}{v_3}\right) + c_v\left(T_2 - T_1\right)$$

$$= RT_1 \; In\left(\frac{v_2}{v_1}\right) + RT_2 \; In\left(\frac{v_4}{v_3}\right) \qquad (18.10)$$

Energy absorbed as heat

$$Q_1 = RT_1 \; In \; \left(v_2 / v_1\right) \qquad (18.11)$$

Thermal efficiency,

$$\eta = 1 + \frac{RT_2 \; In\left(v_4 / v_3\right)}{RT_1 \; In\left(v_2 / v_1\right)} \qquad (18.12)$$

Here, for the ideal gases we can write

$$\frac{T_2}{T_1} = \left(\frac{v_2}{v_3}\right)^{\gamma - 1}$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_4}\right)^{\gamma - 1}$$

Also,

$$\frac{v_2}{v_3} = \frac{v_1}{v_4}$$

or,

$$\frac{v_2}{v_1} = \frac{v_3}{v_4} \tag{18.13}$$

So,

$$\eta = 1 - \frac{T_2 \; ln(v_2 / v_1)}{T_1 \; ln(v_2 / v_1)} = 1 - \frac{T_2}{T_1} \tag{18.14}$$

Carnot's Principles (Theorems)

Two consequences of the second law of thermodynamics are well known as Carnot's principles.

Principle I:

No heat engine operating between the two given thermal reservoirs, each of which is maintained at a constant temperature, can be more efficient than a reversible engine operating between the same two thermal reservoirs. Refer to Figure 19.1

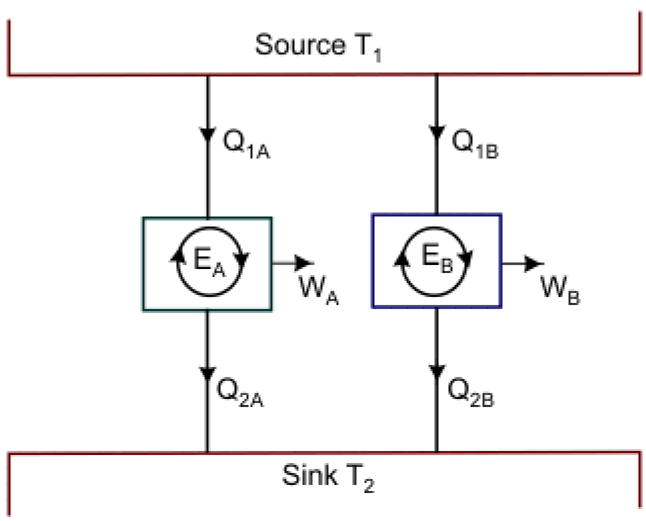

Figure 19.1

Let two heat engines E_A and E_B operate between the given source at temperature T_1 and the given sink at temperature T_2 as shown.

Let E_A be any heat engine and E_B any reversible heat engine. We are to prove that the efficiency of E_B is more than that of E_A. Let us assume that it is not true $\eta_A > \eta_B$. Let the rates of working of the engines be such that

$$Q_{1A} = Q_{1B} = Q_1 \qquad (19.1)$$

Since,

$$\eta_A > \eta_B \Rightarrow \frac{W_A}{Q_{1A}} > \frac{W_B}{Q_{1B}}; \quad or, \quad W_A > W_B \qquad (19.2)$$

Now let the direction of E_B be reversed.

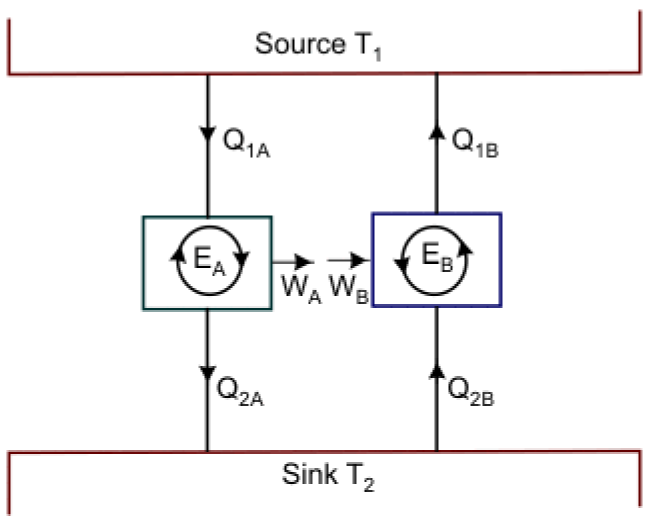

Figure 19.2

Refer to Figure 19.2. Since E_B is a reversible heat engine, the magnitudes of heat and work quantities will remain the same, but their directions will be reversed as shown.

Since $W_A > W_B$ some part of W_A (equal to W_B) may be fed to drive the reversed heat engine E_B. Since, $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by the reversed E_B may be supplied to E_A.

The source may, therefore, be eliminated. The net result is that E_A and E_B together constitute a heat engine which, operating in a cycle, produces net work $W_A - W_B$, while exchanging heat with a single reservoir at T_2.

This violates the Kelvin-Planck statement of the second law. Hence the assumption $\eta_A > \eta_B$ is wrong.

Therefore,

$$\eta_B \geq \eta_A \qquad (19.3)$$

Two consequences of the second law of thermodynamics are well known as Carnot's principles.

Principle I:

No heat engine operating between the two given thermal reservoirs, each of which is maintained at a constant temperature, can be more efficient than a reversible engine operating between the same two thermal reservoirs. Refer to Figure 19.1

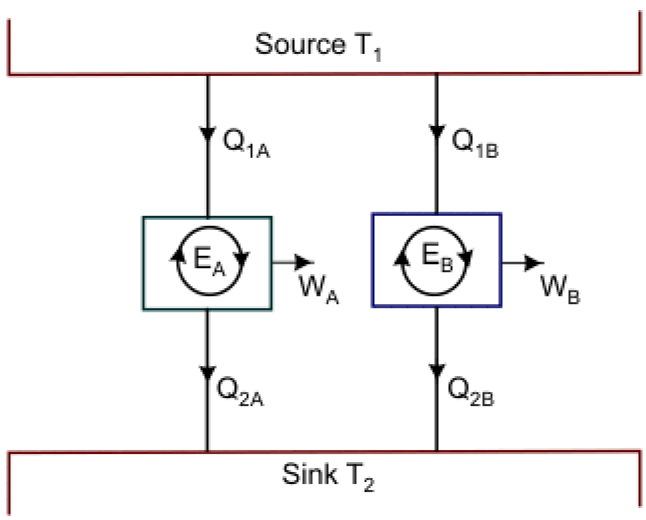

Figure 19.1

Let two heat engines E_A and E_B operate between the given source at temperature T_1 and the given sink at temperature T_2 as shown.

Let E_A be any heat engine and E_B any reversible heat engine. We are to prove that the efficiency of E_B is more than that of E_A. Let us assume that it is not true $\eta_A > \eta_B$. Let the rates of working of the engines be such that

$$Q_{1A} = Q_{1B} = Q_1 \qquad (19.1)$$

Since,

$$\eta_A > \eta_B \Rightarrow \frac{W_A}{Q_{1A}} > \frac{W_B}{Q_{1B}}; \quad or, \quad W_A > W_B \qquad (19.2)$$

Now let the direction of E_B be reversed.

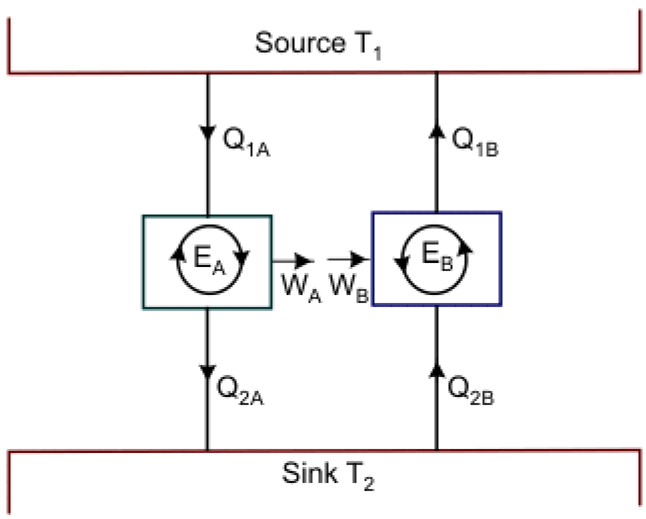

Figure 19.2

Refer to Figure 19.2. Since E_B is a reversible heat engine, the magnitudes of heat and work quantities will remain the same, but their directions will be reversed as shown.

Since $W_A > W_B$ some part of W_A (equal to W_B) may be fed to drive the reversed heat engine E_B. Since, $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by the reversed E_B may be supplied to E_A.

The source may, therefore, be eliminated. The net result is that E_A and E_B together constitute a heat engine which, operating in a cycle, produces net work $W_A - W_B$, while exchanging heat with a single reservoir at T_2.

This violates the Kelvin-Planck statement of the second law. Hence the assumption $\eta_A > \eta_B$ is wrong.

Therefore,

$$\eta_B \geq \eta_A \qquad (19.3)$$

Principle II:

All reversible heat engines operating between the two given thermal reservoirs have the same efficiency. The efficiency of reversible heat engine does not depend on the working fluid, it depends only on the temperature of the reservoirs between which it operates.

To prove the proposition, let us assume that the efficiency of the reversible engine R_1 is greater than the efficiency of the reversible engine R_2.

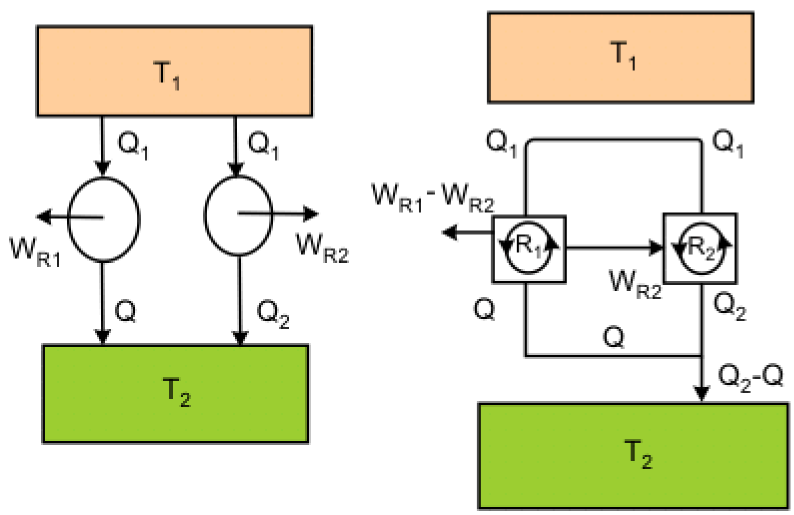

Figure 19.3

Refer to Figure 19.3. The engine R_1 absorbs energy as heat Q_1 from the constant temperature thermal reservoir at T_1, does work W_{R1} and rejects energy as heat Q to the reservoir at T_2. The engine R_2 absorbs energy as heat Q_1 from the reservoir at T_1, does work W_{R2} and rejects energy as heat Q_2 to the reservoir at T_2. Then $W_{R1} = Q_1 - Q$, and $W_{R2} = Q_1 - Q_2$

$$\eta_{R1} = W_{R1} / Q_1 = 1 - \frac{Q}{Q_1} \qquad (19.4)$$

And

$$\eta_{R2} = W_{R2} / Q_1 = 1 - \frac{Q_2}{Q_1} \tag{19.5}$$

By assumption, $\eta_{R1} > \eta_{R2}$

Then,

$$\left(1 - \frac{Q}{Q_1}\right) > \left(1 - \frac{Q_2}{Q_1}\right) \quad or \quad Q < Q_2 \tag{19.6}$$

Therefore, $W_{R1} > W_{R2}$

Since R_2 is a reversible engine, it can be made to execute the cycle in the reversed order. That is, when work W_{R2} is performed on the device, it absorbs energy as heat, Q_2 from the reservoir at T_2 and rejects energy as heat Q_1 to the reservoir at T_1. Since, $W_{R1} > W_{R2}$, R_2 can be run as a heat pump utilizing **part of the work done by** R_1. The combination of the two devices is also shown in the figure.

The net work done by the device is given by

$$W_{R1} - W_{R2} = (Q_1 - Q) - (Q_1 - Q_2) = Q_2 - Q \tag{19.7}$$

- The resulting device absorbs energy as heat $(Q_2 - Q)$ from the reservoir at T_2.
- Does not require any interaction with the second reservoir.
- Delivers an equivalent amount of work.

This is in violation of the Kelvin-Planck statement of the second law of thermodynamics. Hence the assumption that $\eta_{R1} > \eta_{R2}$, is incorrect. Therefore,

$$\eta_{R2} \geq \eta_{R1} \tag{19.8}$$

Nov let us assume that the reversible engine R_2 is more efficient then the reversible engine R_1. Then the reversible engine R_1 can be run as a heat pump, utilizing the part of the work done by R_2. By following the similar argument as the earlier case, we can arrive at the result that,

$$\eta_{R1} \geq \eta_{R2} \tag{19.9}$$

Hence, it can be concluded that

$$\eta_{R1} = \eta_{R2} \tag{19.10}$$

Stated in works: All reversible engines operating between the two given thermal reservoirs have the same efficiency.