Salahaddin University-Erbil

College of Engineering

Chemical and Petrochemical Department

Engineering Thermodynamics-I

Hardi A. Siwaily

M.Sc. Mechanical Engineering- Thermal Power.

Second Law of Thermodynamics and Entropy

It has been observed that *energy can flow* from a system in the form of *heat* or *work*.

- The first law of thermodynamics sets no limit to the amount of the total energy of a system which can be caused to flow out as work.
- A limit is imposed, however, as a result of the principle enunciated in the second law of thermodynamics which states that heat will flow naturally from one energy reservoir to another at a lower temperature, but not in opposite direction without assistance.
- This is very important because a heat engine operates between two energy reservoirs at different temperatures.
- Further the first law of thermodynamics *establishes equivalence between the quantity of heat used and the 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*.
- This gap has been *bridged* by the second law of thermodynamics.

PERFORMANCE OF HEAT ENGINES AND REVERSED HEAT ENGINES

Refer Fig.1 (*a*). A *heat engine* is used to produce the maximum work transfer from a given positive heat transfer. The measure of success is called the *thermal efficiency* of the engine and is defined by the ratio :

$$\text{Thermal efficiency, } \eta_{th} = \frac{W}{Q_1}$$

where,

W = Net work transfer from the engine, and

Q_1 = Heat transfer to engine.

For a *reversed heat engine* [Fig.1 (*b*)] acting as a *refrigerator* when the purpose is to achieve the maximum heat transfer from the cold reservoir, the measure of success is called the *co-efficient of performance* (C.O.P.). It is defined by the ratio :

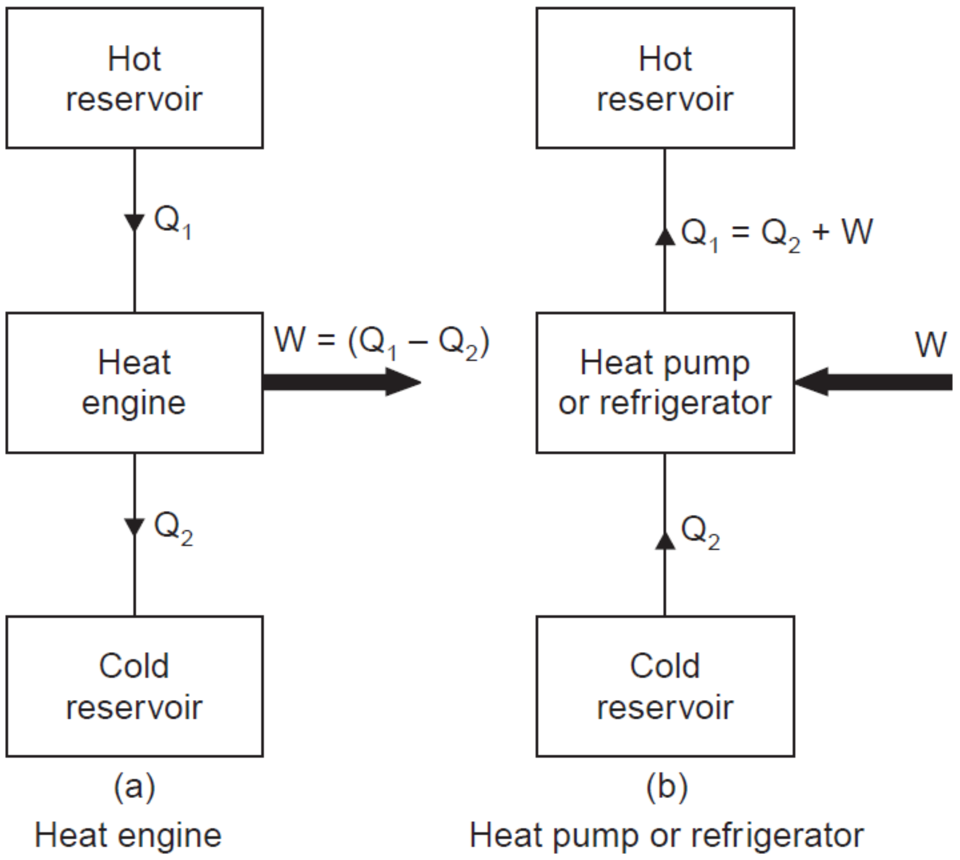

Fig.1

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$$\text{Co-efficient of performance, } (\text{C.O.P.})_{ref.} = \frac{Q_2}{W}$$

where, Q_2 = Heat transfer *from cold reservoir*, and
W = The net work transfer to the refrigerator.

For a **reversed heat engine** [Fig. (*b*)] acting as a *heat pump*, the measure of success is again called the *co-efficient of performance*. It is defined by the ratio :

$$\text{Co-efficient of performance, } (\text{C.O.P.})_{heat\ pump} = \frac{Q_1}{W}$$

where, Q_1 = Heat transfer *to hot reservoir*, and
W = Net work transfer to the heat pump.

$$\eta_{th} = \frac{Q_1 - Q_2}{Q_1}$$

$$(C.O.P.)_{ref} = \frac{Q_2}{Q_1 - Q_2}$$

$$(C.O.P.)_{heat\ pump} = \frac{Q_1}{Q_1 - Q_2}$$

In all the above three cases application of the first law gives the relation $Q_1 - Q_2 = W$, and this can be used to rewrite the expressions for thermal efficiency and co-efficient of performance solely in terms of the heat transfers.

It may be seen that $\boldsymbol{\eta_{th}}$ is *always* ***less than unity*** and (***C.O.P.***) *heat pump* is *always* ***greater than unity***.

Second Law of Thermodynamics and Entropy

STATEMENTS OF SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics has been enunciated meticulously by Clausius, Kelvin and Planck in slightly different words although both statements are basically identical. Each statement is based on an *irreversible process*. The *first considers transformation of heat between two thermal reservoirs* while the *second considers the transformation of heat into work.*

Clausius Statement

"*It is impossible for a self acting machine working in a cyclic process unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature*".

In other words, heat of, itself, cannot flow from a colder to a hotter body.

Kelvin-Planck Statement

"*It is impossible to construct an engine, which while operating in a cycle produces no other effect except to extract heat from a single reservoir and do equivalent amount of work*".

Although the Clausius and Kelvin-Planck statements appear to be different, they are really equivalent in the sense that a *violation of either statement implies violation of other*.

Second Law of Thermodynamics and Entropy

Equivalence of Clausius Statement to the Kelvin-Planck Statement

Refer to the following Fig.2 Consider a higher temperature reservoir T_1 and low temperature reservoir T_2. Fig.2 shows a heat pump which requires no work and transfers an amount of Q_2 from a low temperature to a higher temperature reservoir (in violation of the Clausius statement). Let an amount of heat Q_1 (greater than Q_2) be transferred from high temperature reservoir to heat engine which develops a net work, $W = Q_1 - Q_2$ and rejects Q_2 to the low temperature reservoir. Since there is no heat interaction with the low temperature, it can be eliminated.

of the heat engine and heat pump acts then like a heat engine exchanging heat with a single reservoir, which is the violation of the Kelvin-Planck statement.

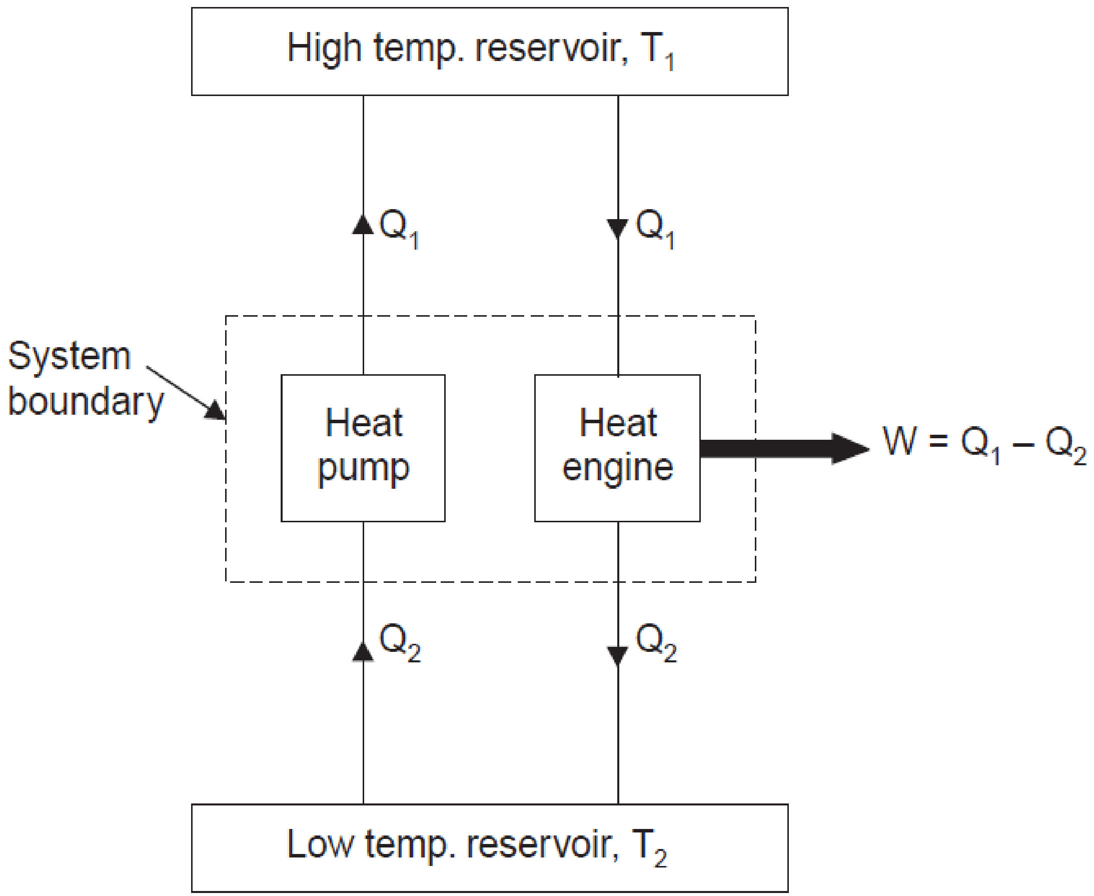

Fig.2. Equivalence of Clausius statement to Kelvin-Planck statement.

THERMODYNAMIC TEMPERATURE

Take the case of reversible heat engine operating between two reservoirs. Its thermal efficiency is given by

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

The temperature of a reservoir remains uniform and fixed irrespective of heat transfer. This means that reservoir has only one property defining its state and the heat transfer from a reservoir is some function of that property, *temperature*. Thus $Q = \varphi\,(K)$, where K is the temperature of reservoir. The choice of the function is universally accepted to be such that the relation,

$$\frac{Q_1}{Q_2} = \frac{\phi(K_1)}{\phi(K_2)} \text{ becomes } \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

where T_1 and T_2 are the thermodynamic temperatures of the reservoirs. Zero thermodynamic temperature (that temperature to which T_2 tends, as the heat transfer Q_2 tends to zero) has never been attained and *one form of third law of thermodynamics is the statement* :

Second Law of Thermodynamics and Entropy

The temperature of a system cannot be reduced to zero in a finite number of processes

After establishing the concept of a zero thermodynamic temperature, a reference reservoir is chosen and assigned a numerical value of temperature. Any other thermodynamic temperature may now be defined in terms of reference value and the heat transfers that would occur with reversible engine,

$$T = T_{ref.} \frac{Q}{Q_{ref.}}$$

The determination of thermodynamic temperature cannot be made in this way as it is not possible to build a reversible engine. Temperatures are determined by the application of thermodynamic relations to other measurements.

CLAUSIUS INEQUALITY

When a reversible engine uses more than two reservoirs the third or higher numbered reservoirs will not be equal in temperature to the original two. Consideration of expression for efficiency of the engine indicates that for maximum efficiency, all the heat transfer should take place at maximum or minimum reservoir temperatures. Any intermediate reservoir used will, therefore, lower the efficiency of the heat engine. Practical engine cycles often involve continuous changes of temperature during heat transfer.

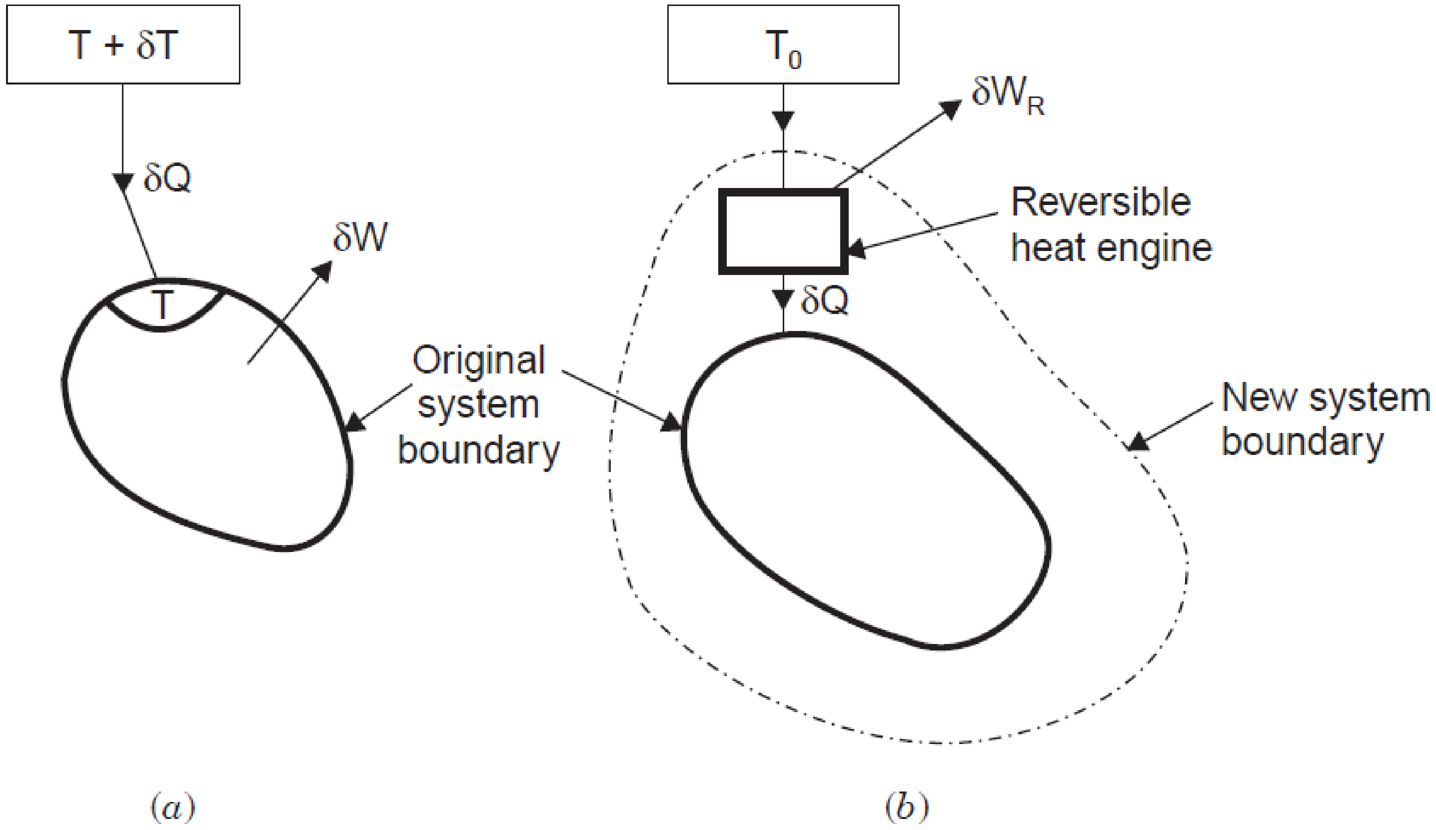

Fig. 3. The Clausius inequality.

CARNOT CYCLE

The cycle was first suggested by a French engineer Sadi Carnot in 1824 which works on reversible cycle and is known as *Carnot cycle*.

Any fluid may be used to operate the Carnot cycle (Fig.4) which is performed in an engine cylinder the head of which is supposed alternatively to be perfect conductor or a perfect insulator of a heat. Heat is caused to flow into the cylinder by the application of high temperature energy source to the cylinder head during expansion, and to flow from the cylinder by the application of a lower temperature energy source to the head during compression.

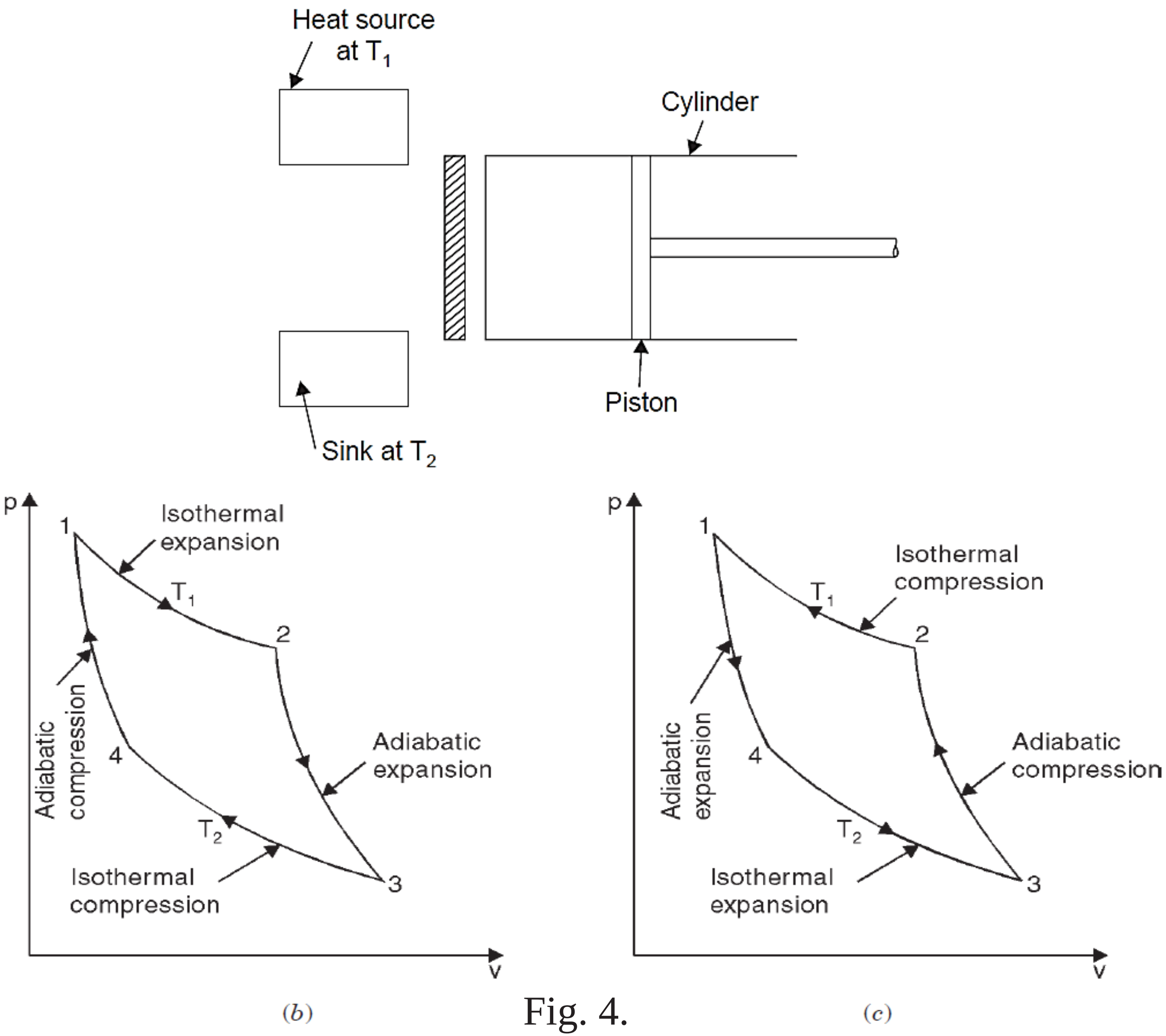

Fig. 4.

Second Law of Thermodynamics and Entropy

- The ***assumptions*** made for describing the working of the Carnot engine are as follows :

(*i*) The piston moving in a cylinder is **Frictionless**.

(*ii*) The cylinder wall is **perfect insulators of heat**.

(*iii*) The cylinder head is a **perfect heat conductor**.

(*iv*) The **transfer of heat does not affect the temperature of source or sink**.

(*v*) Working Fluid is a **perfect gas and has constant specific heat**.

(*vi*) **Compression and expansion are reversible**.

Second Law of Thermodynamics and Entropy

Following are the *four stages* of Carnot cycle :

Stage 1. (Process 1-2). Hot energy source is applied. Heat Q_1 is taken in whilst the fluid expands isothermally and reversibly at constant high temperature T_1.

Stage 2. (Process 2-3). The cylinder becomes a perfect insulator so that no heat flow takes place. The fluid expands adiabatically and reversibly whilst temperature falls from T_1 to T_2.

Stage 3. (Process 3-4). Cold energy source is applied. Heat Q_2 flows from the fluid whilst it is compressed isothermally and reversibly at constant lower temperature T_2.

Stage 4. (Process 4-1). Cylinder head becomes a perfect insulator so that no heat flow occurs. The compression is continued adiabatically and reversibly during which temperature is raised from T_2 to T_1.

$$W = Q_1 - Q_2$$

Also, thermal efficiency, $$\eta_{th} = \frac{\text{Work done}}{\text{Heat supplied by the source}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \left(= 1 - \frac{T_2}{T_1} \right)$$

$$\left[\begin{array}{c} \because \quad Q_1 = m\, c_p\, T_1 \\ Q_2 = m\, c_p\, T_2 \\ \text{where, } m = \text{mass of fluid.} \end{array} \right]$$

Second Law of Thermodynamics and Entropy

CARNOT'S THEOREM

"It states that of all engines operating between a given constant temperature source and a given constant temperature sink, none has a higher efficiency than a reversible engine".

HE_A and HE_B are the two engines operating between the given source at temperature T_1 and the given sink at temperature T_2.

Let HE_A be *any* heat engine and HE_B be *any reversible* heat engine. We have to prove that efficiency of HE_B is more than that of HE_A. Let us assume that $\eta_A > \eta_B$. Let the rates of working of the engines be such that

$$Q_{1A} = Q_{1B} = Q_1$$

Since

$$\eta_A > \eta_B$$

$$\frac{W_A}{Q_{1A}} > \frac{W_B}{Q_{1B}}$$

$$\therefore \quad W_A > W_B$$

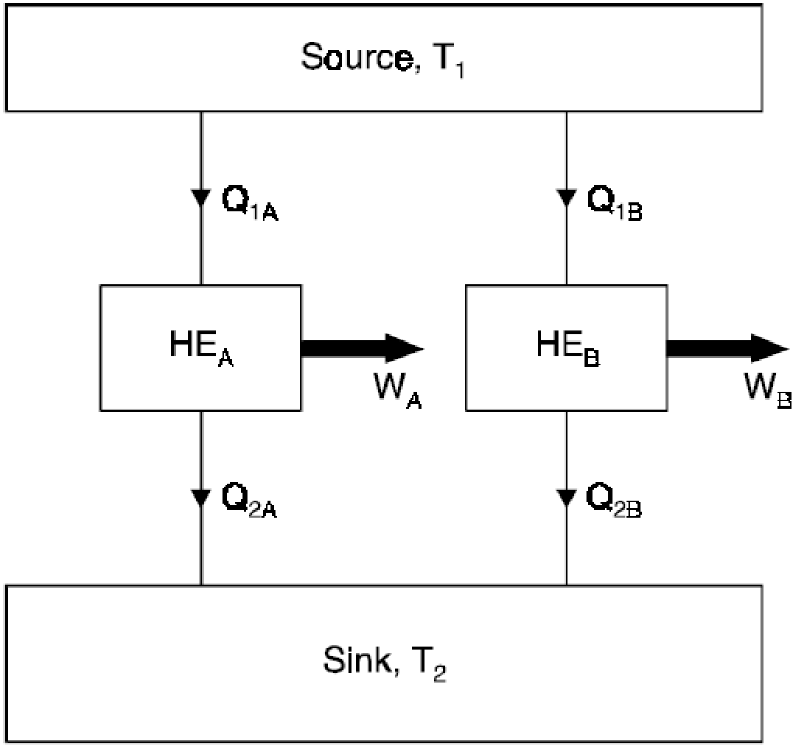

Fig. 5. Two cyclic heat engines HE_A and HE_B operating between the same source and sink, of which HE_B is reversible.

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Now, let HE_B be reversed. Since HE_B is a reversible heat engine, the magnitudes of heat and work transfer quantities will remain the same, but their directions will be reversed, as shown in Fig. 6. Since $W_A > W_B$, some part of W_A (equal to W_B) may be fed to drive the reversed heat engine HE_B. Since $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by HE_B may be supplied to HE_A. The source may, therefore, be eliminated (Fig. 7).

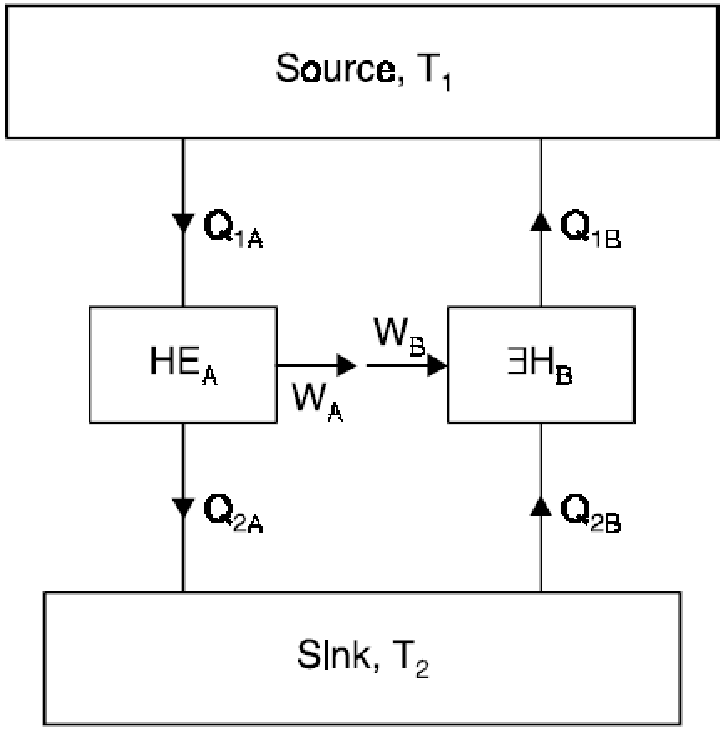


Fig. 6. HE_B is reversed.

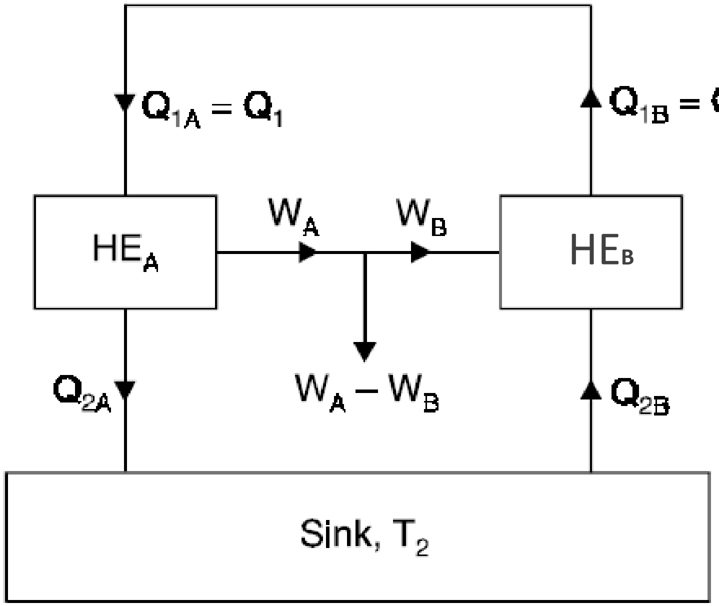


Fig. 7. HE_A and HE_B together violate the Kelvin-Planck statement. $\therefore \eta_B \geq \eta_A$.

EFFICIENCY OF THE REVERSIBLE HEAT ENGINE

The efficiency of a reversible heat engine in which heat is received solely at T_1 is found to be

$$\eta_{rev.} = \eta_{max} = 1 - \left(\frac{Q_2}{Q_1}\right)_{rev.} = 1 - \frac{T_2}{T_1}$$

$$\eta_{rev.} = \frac{T_1 - T_2}{T_1}$$

From the above expression, it may be noted that as T_2 decreases and T_1 increases, the efficiency of the reversible cycle increases.

Since η is always less than unity, T_2 is always greater than zero and + ve. The C.O.P. of a refrigerator is given by

$$(\text{C.O.P.})_{ref.} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

For a *reversible refrigerator*, using

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

$$(\text{C.O.P.})_{rev.} = \frac{1}{\frac{T_1}{T_2} - 1}$$

$$\therefore \qquad [(\text{C.O.P.})_{ref.}]_{rev.} = \frac{T_2}{T_1 - T_2}$$

Similarly, for a *reversible heat pump*

$$[(\text{C.O.P.})_{heat\ pump}]_{rev.} = \frac{T_1}{T_1 - T_2}$$

Examples

1/ A heat engine receives heat at the rate of 1500 kJ/min and gives an output of 8.2 kW. Determine :

(i) *The thermal efficiency ;*

(ii) *(ii) The rate of heat rejection.*

Solution. Heat received by the heat engine,

$$Q_1 = 1500 \text{ kJ/min}$$

$$= \frac{1500}{60} = 25 \text{ kJ/s}$$

Work output, $W = 8.2 \text{ kW} = 8.2 \text{ kJ/s}.$

(*i*) Thermal efficiency, $\eta_{th} = \dfrac{W}{Q_1}$

$$= \frac{8.2}{25} = 0.328 = 32.8\%$$

Hence, **thermal efficiency = 32.8%. (Ans.)**

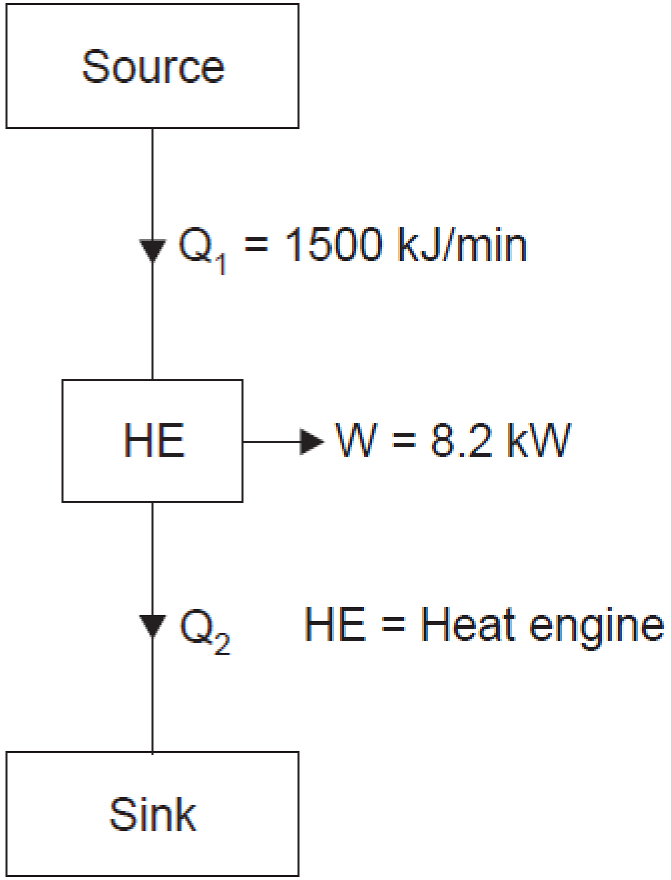
(*ii*) Rate of heat rejection,

$$Q_2 = Q_1 - W = 25 - 8.2$$

$$= 16.8 \text{ kJ/s}$$

Hence, **the rate of heat rejection = 16.8 kJ/s.**

(Ans.)



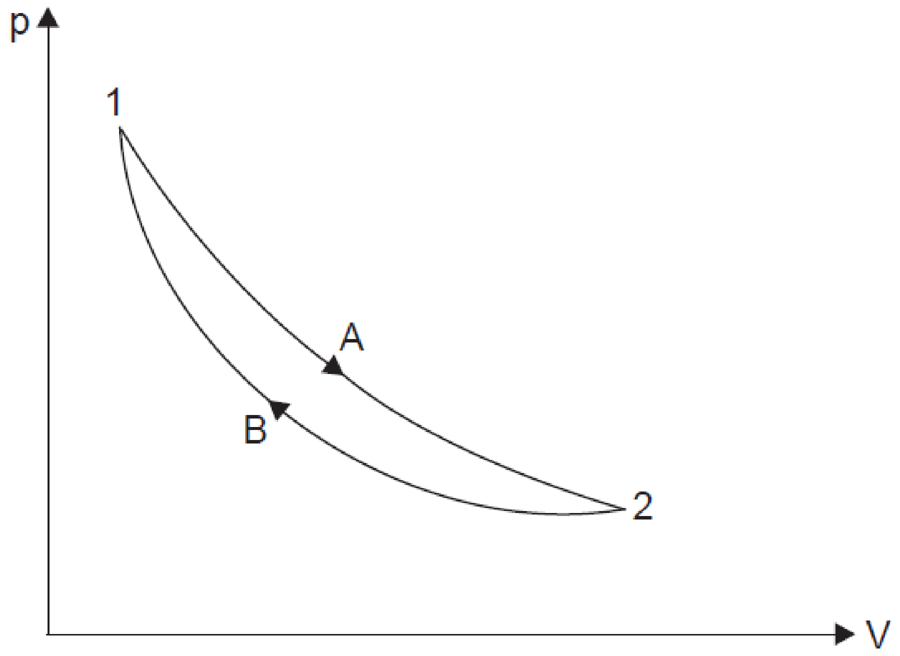
Examples

2/ During a process a system receives 30 kJ of heat from a reservoir and does 60 kJ of work. Is it possible to reach initial state by an adiabatic process ?

Solution:

Heat received by the system = 30 kJ

Work done = 60 kJ



Process 1-2 : By first law of thermodynamics,

$$Q_{1-2} = (U_2 - U_1) + W_{1-2}$$

$$30 = (U_2 - U_1) + 60 \qquad \therefore \qquad (U_2 - U_1) = -30 \text{ kJ.}$$

Process 2-1 : By first law of thermodynamics,

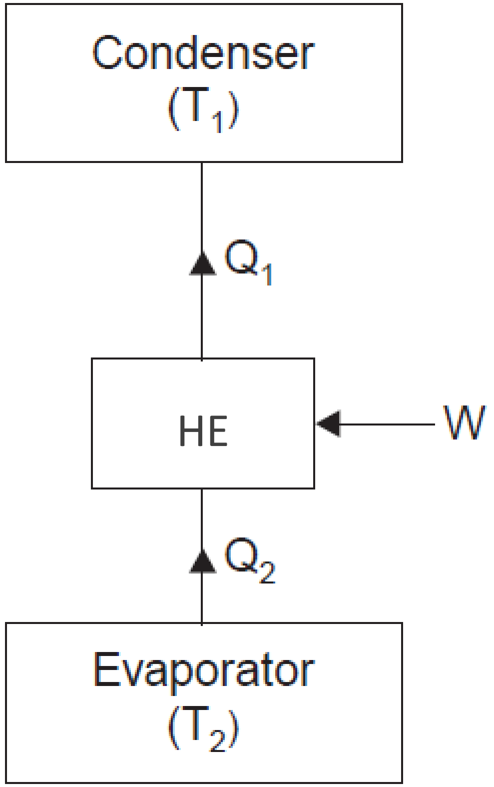
$$Q_{2-1} = (U_1 - U_2) + W_{2-1}$$

$$\therefore \qquad 0 = 30 + W_{2-1} \qquad \therefore \qquad W_{2-1} = -30 \text{ kJ.}$$

Thus 30 kJ work has to be done *on the system* to restore it to original state, by adiabatic process.

Examples

3/ Find the co-efficient of performance and heat transfer rate in the condenser of a refrigerator in kJ/h which has a refrigeration capacity of 12000 kJ/h when power input is 0.75 kW.



Solution:

Refrigeration capacity, Q_2 = 12000 kJ/h

Power input, W = 0.75 kW (= 0.75 × 60 × 60 kJ/h)

Co-efficient of performance, C.O.P. :

Heat transfer rate :

$$(\text{C.O.P.})_{refrigerator} = \frac{\text{Heat absorbed at lower temperature}}{\text{Work input}}$$

$$\therefore \quad \text{C.O.P.} = \frac{Q_2}{W} = \frac{12000}{0.75 \times 60 \times 60} = 4.44$$

Hence **C.O.P. = 4.44. (Ans.)**

Hence transfer rate in condenser = Q_1

According to the first law

$Q_1 = Q_2 + W = 12000 + 0.75 \times 60 \times 60 = 14700$ kJ/h

Hence, **heat transfer rate = 14700 kJ/h. (Ans.)**

End