

Limitations of the first law:-

- 1). The first law does not show whether or not a system will undergo a change. Simply it states that heat and work are mutually convertible during a process.
- 2). The first law does not predict what portion of heat transferred can be converted into useful work. According to this law, probably all the heat transferred could be converted into work. However, in practice much heat is wasted in the process. Thus the process of converting heat completely into work is impossible, but it is possible to convert work completely into heat.
- 3). The first law does not specify the direction of heat and work.

Thermal Energy Reservoir (TER) :- TER is defined as a large body of infinite heat capacity, which is capable of absorbing or rejecting an unlimited quantity of heat without suffering appreciable changes in its thermodynamic coordinates. The changes that do take place in the large body as heat enters or leaves are so very slow and so very minute that all processes within it are quasi-static.

Source - The thermal energy reservoir  $TER_H$  from which heat  $Q_1$  is

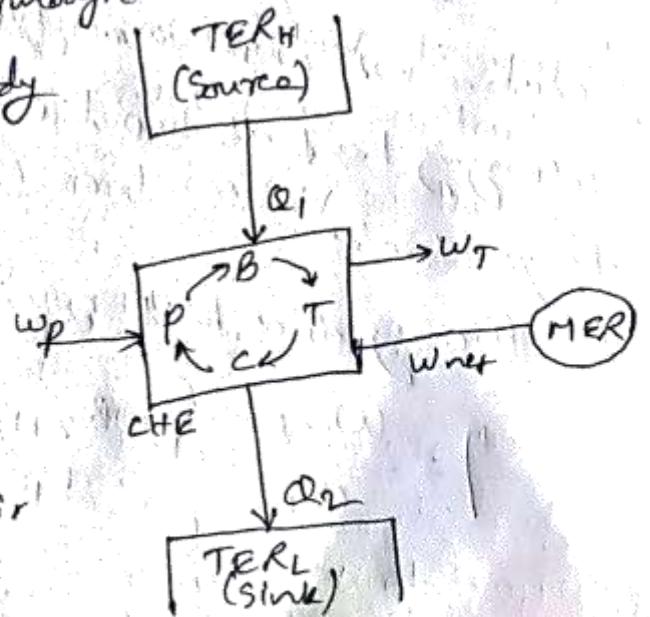


Fig: Cyclic heat engine (CHE) with source and sink.

transferred to the system operating in a heat engine cycle is called the source.

Ex:- A typical source is a constant temperature furnace where fuel is continuously burnt.

Sink - The thermal energy reservoir (TER) to which heat  $Q_2$  is rejected from the system during a cycle is the sink.

Ex:- A typical sink is a river or sea or the atmosphere itself.

Mechanical Energy Reservoir (MER) is a large body enclosed by an adiabatic impermeable wall capable of storing work as potential energy (such as a raised weight or wound spring) or kinetic energy (such as a rotating flywheel). All processes of interest within an MER are essentially quasi-static. An MER receives and delivers mechanical energy quasi-statically.

Heat engine: Figure shows heat engine producing net work in a cycle by exchanging heat at two different temperatures.

The efficiency of a heat engine

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

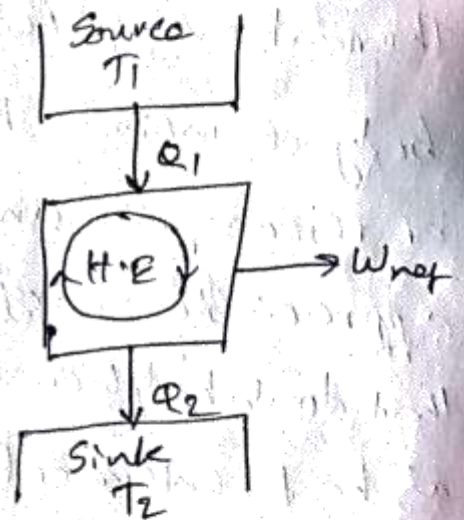
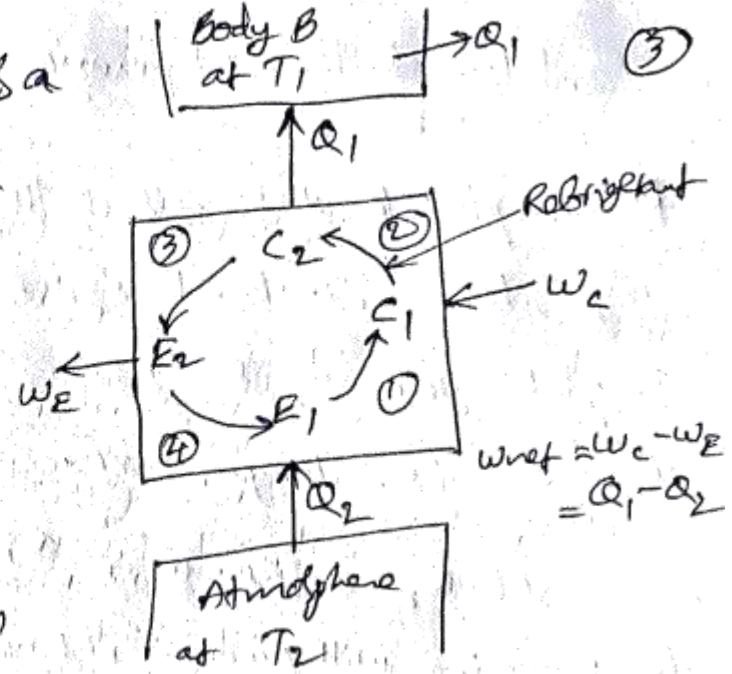


Fig: Heat engine

Heat pump:- A heat pump is a device which, operating in a cycle, maintains a body, say B, at a temperature higher than the temperature of the surroundings.



The heat is extracted from the low temperature reservoir (atmosphere), and discharged into the high temperature body B, with the expenditure of work  $w$  in a cyclic device called a heat pump. The working fluid operates in a cycle flowing through the evaporator  $E_1$ , compressor  $C_1$ , condenser  $C_2$  and expander  $E_2$ , similar to a refrigerator, but the attention is here focussed on the high temperature body B. Here  $Q_1$  and  $w$  are of primary interest, and the COP is defined as

Fig: A cyclic heat pump  
 expenditure of work  $w$  in a cyclic device called a heat pump. The working fluid operates in a cycle flowing through the evaporator  $E_1$ , compressor  $C_1$ , condenser  $C_2$  and expander  $E_2$ , similar to a refrigerator, but the attention is here focussed on the high temperature body B. Here  $Q_1$  and  $w$  are of primary interest, and the COP is defined as

Coefficient of performance, 
$$COP = \frac{Q_1}{w} = \frac{Q_1}{Q_1 - Q_2}$$

$$\therefore (COP)_{HP} = \frac{Q_1}{Q_1 - Q_2}$$

## Second law of thermodynamics :-

(4)

Kelvin-Planck statement of the second law states: "It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single fixed temperature."

If  $Q_2 = 0$  (i.e.  $w_{net} = Q_1$ , or  $\eta = 100$ ), the heat engine will produce net work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement (Fig). Such a heat engine is called a perpetual motion machine of the second kind (PMM2). A PMM2 is impossible.

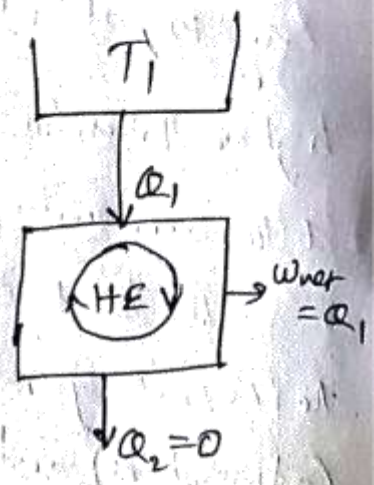


Fig: A PMM2

## Clausius statement of the second law:- "It is impossible to

construct a device, which, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body."

Heat cannot flow of itself from a body at a lower temperature to a body at a higher temperature. Some work must be expended to achieve this.

Heat always flows from a body at a higher temperature to a body at a lower temperature. The reverse process never occurs spontaneously.

# Equivalence of kelvin - planck and clausius statements: ⑤

At first sight, kelvin - planck's and clausius's statements may appear to be unconnected, but it can easily be shown, that they are virtually two parallel statements of the second law and are equivalent in all respects.

The Equivalence of the two statements will be proved if it can be shown that the violation of one statement implies the violation of the second, and vice versa.

a) Let us first consider a cyclic heat pump  $P$  which transfers heat from a low temperature reservoir ( $T_2$ ) to a high temperature reservoir ( $T_1$ ) with no other effect, i.e. with no expenditure of work, violating clausius statement.

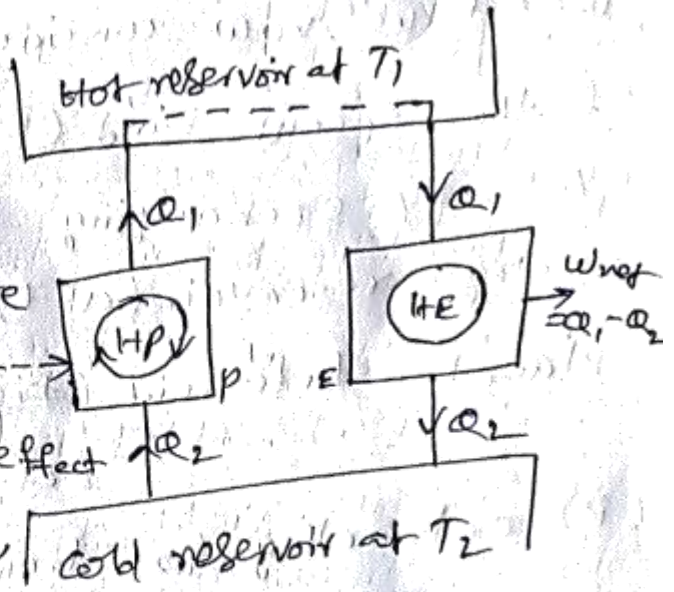


Fig: Violation of the clausius statement

Let us assume a cyclic heat engine  $E$  operating between the same thermal energy reservoirs, producing  $W_{net}$  in one cycle. The rate of working of the heat engine is such that it draws an amount of heat  $Q_1$  from the hot reservoir equal to that discharged by the heat pump.

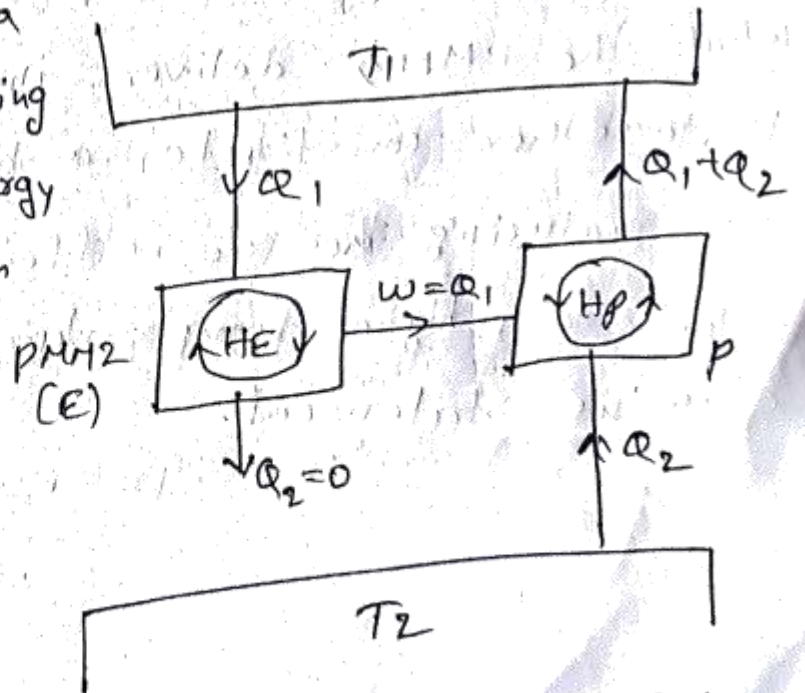


Fig: Violation of the kelvin - planck statement

Then the hot reservoir may be eliminated and the heat  $Q_1$  discharged by the heat pump is fed to the heat engine. So we see that the heat pump P and the heat engine E acting together constitute a heat engine operating in cycles and producing net work while exchanging heat only with one body at a single fixed temperature. This violates the Kelvin-Planck statement.

(b) Let us now consider a perpetual motion machine of the second kind (E) which produces net work in a cycle by exchanging heat with only one thermal energy reservoir (at  $t_2$ ) and thus violates the Kelvin-Planck statement ~~(Fig. 6.10)~~

Let us assume a cyclic heat pump (P) extracting  $Q_2$  from a low temperature reservoir at  $t_2$  and discharging heat to the high temperature reservoir at  $t_1$  with the expenditure of work  $W$  equal to what the PMM 2 delivers in a complete cycle. So E and P together constitute a heat pump working in cycle and producing the sole effect of transferring heat from a lower to a higher temperature body, thus violating the Clausius statement.

CARNOT'S THEOREM: (7)

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

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 in Fig.

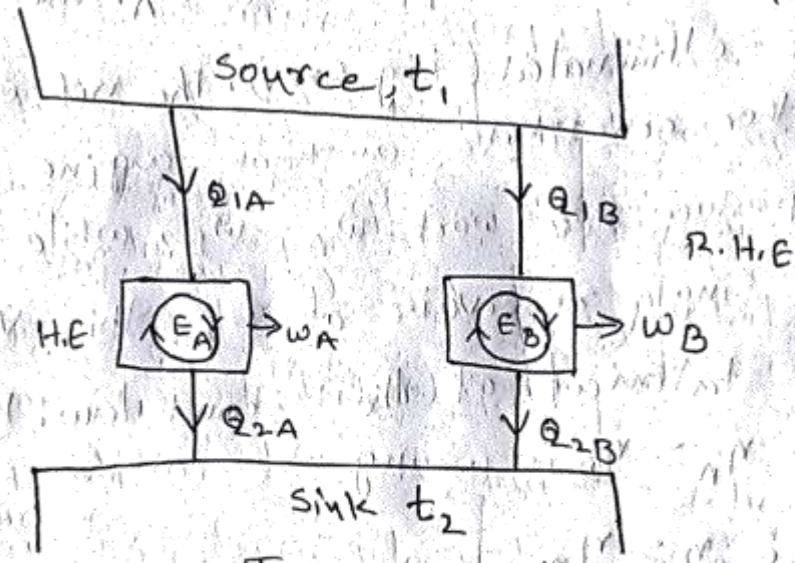


Fig. Two cyclic Heat Engines  $E_A$  and  $E_B$  operating between the same source and sink, of which  $E_B$  is Reversible

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

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

$$\eta_A > \eta_B$$

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

$$W_A > W_B$$

(1) Now, let  $E_B$  be reversed. Since  $E_B$  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 6.26. Since  $W_A > W_B$ , some part of  $W_A$  (equal to  $W_B$ ) may be fed to drive that reversed heat engine  $E_B$ . Since  $Q_{1A} = Q_{1B} = Q_1$ , the heat discharged by  $E_B$  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 that Kelvin-Planck statement of the second law. Hence the assumption that  $\eta_A > \eta_B$  is wrong.

Therefore  $\eta_B \geq \eta_A$

Second Law of Thermodynamics

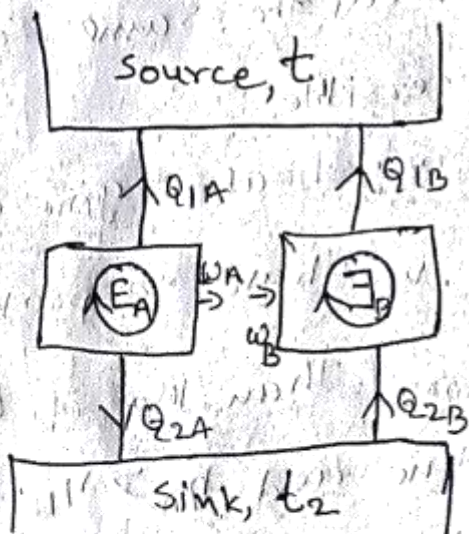


Fig. 6.26  $E_B$  is Reversed

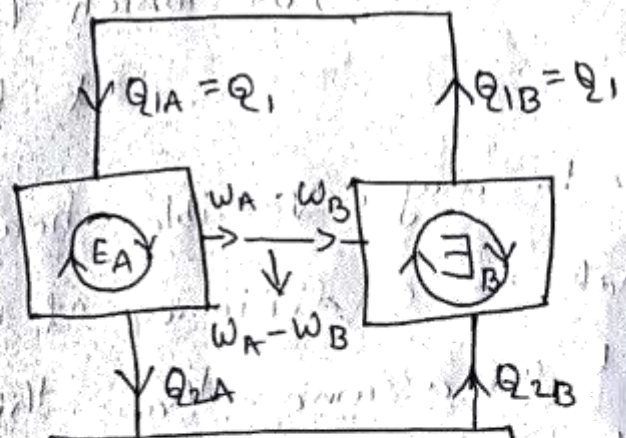


Fig. 6.27  $E_A$  and  $E_B$  together violate the K-P statement.



## COROLLARY OF CARNOT'S THEOREM (a)

(1) The efficiency of all reversible heat engines operating between the same temperature levels is the same.

(2) Let both the heat engines  $E_A$  and  $E_B$  (Fig 6.25) be reversible. Let us assume  $\eta_A > \eta_B$ . Similar to the procedure outlined in the preceding article, if  $E_B$  is reversed to run, say, as a heat pump using some part of the work output ( $W_A$ ) of engine  $E_A$ , we see that the combined system of heat pump  $E_B$  and engine  $E_A$ , becomes a PMM2. So  $\eta_A$  cannot be greater than  $\eta_B$ . Similarly, if we assume  $\eta_B > \eta_A$  and reverse the engine  $E_A$ , we observe that  $\eta_B$  cannot be greater than  $\eta_A$ .

Therefore  $\eta_A = \eta_B$

(3) Since the efficiencies of all reversible heat engines operating between the same heat reservoirs are the same, the efficiency of a reversible engine is independent of the nature of amount of the working substance undergoing the cycle.

## ABSOLUTE THERMODYNAMIC TEMPERATURE SCALE

The efficiency of any heat engine receiving heat  $Q_1$  and rejecting heat  $Q_2$  is given by

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (6.18)$$

By the second law it is necessary to have a temperature difference ( $t_1 - t_2$ ) to obtain work for any

cycle. We know that the efficiency to all heat engines operating between the same temperature levels is the same. and it is independent of the working substance. Therefore, for a reversible cycle (Carnot cycle) the efficiency will depend solely upon the temperatures  $t_1$  and  $t_2$ , at which heat is transferred, or

$$\eta_{rev} = f(t_1, t_2) \quad (\text{Carnot})$$

where  $f$  signifies some function of the temperature. From equations (6.18) and

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

In terms of new function  $\frac{Q_1}{Q_2} = F(t_1, t_2) \quad (\text{Carnot})$

If some functional relationship is assigned between  $t_1, t_2$  and  $Q_1/Q_2$ , the equation becomes the definition of a temperature scale.

Let us consider two reversible heat engines,  $E_1$  receiving heat from the source at  $t_1$ , and rejecting heat at  $t_2$  to  $E_2$  which, in turn, rejects heat to the sink at  $t_2$ .

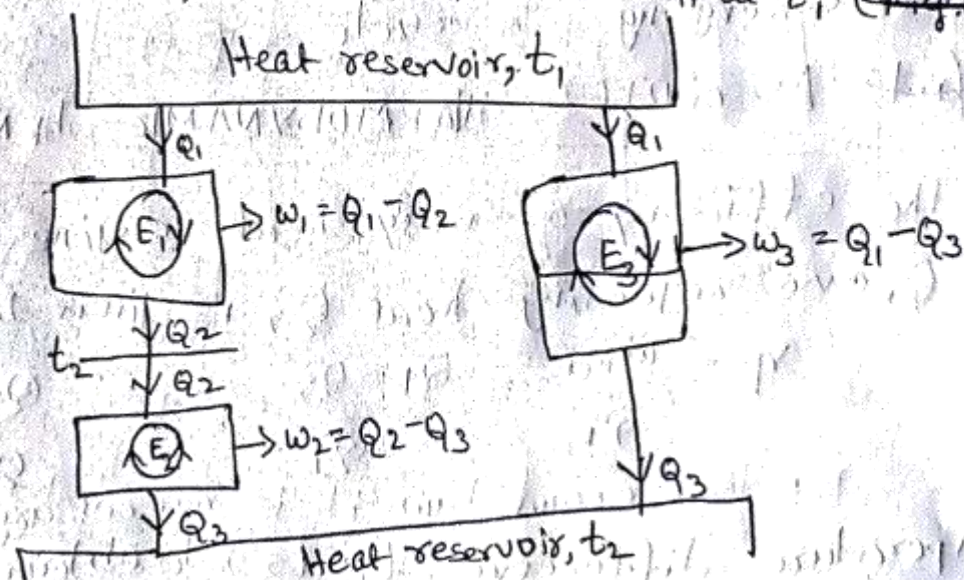


Fig: Three Carnot engines

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

$E_1$  and  $E_2$  together constitute another heat engine  $E_3$ , operating between  $t_1$  and  $t_3$

$\therefore \frac{Q_1}{Q_3} = F(t_1, t_3)$

Now  $\frac{Q_1}{Q_3} = \frac{Q_1/Q_2}{Q_2/Q_3}$

OR  $\frac{Q_1}{Q_2} = F(t_1, t_2) = \frac{F(t_1, t_3)}{F(t_2, t_3)}$  ~~( $\frac{Q_1}{Q_2}$ )~~

The temperatures  $t_1, t_2$  and  $t_3$  are arbitrary.  $t_3$  is chosen. The ratio  $Q_1/Q_2$  depends only on  $t_1$  and  $t_2$  and is independent of  $t_3$ , so  $t_3$  will drop out from the ratio on the right in equation ~~( $\frac{Q_1}{Q_2}$ )~~. After it has been cancelled, the numerator can be written as  $\phi(t_1)$ , and the denominator as  $\phi(t_2)$  where  $\phi$  is another unknown function. Thus

$\frac{Q_1}{Q_2} = F(t_1, t_2) = \frac{\phi(t_1)}{\phi(t_2)}$

Since  $\phi(t)$  is an arbitrary function, the simplest possible way to define the absolute thermodynamic temperature  $T$  is to let  $\phi(t) = T$ , as proposed by Kelvin. Then by definition

$\frac{Q_1}{Q_3} = \frac{T_1}{T_2}$

The absolute thermodynamic temperature scale is also known as the Kelvin scale. Two temperatures

on the kelvin scale bear the same relationship to each other as do the heats absorbed and rejected respectively by a carnot engine operating between two reservoirs at these temperatures. The kelvin temperature scale is, therefore, independent of the peculiar characteristics of any particular substance.

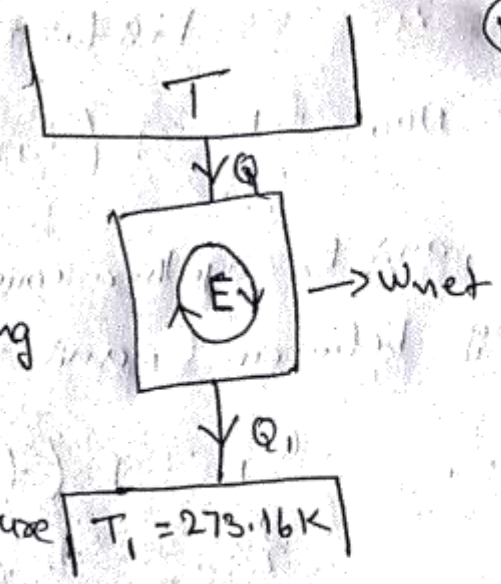


Fig. ~~6.2a~~ carnot Heat engine with sink at Triple point of water.

The heat absorbed  $Q_1$  and heat rejected  $Q_2$  during the two reversible isothermal processes bounded by two reversible adiabatics in a carnot engine can be measured. In defining the kelvin temperature scale also, the triple point of water is taken as the standard reference point. For a carnot engine operating between reservoirs at temperatures  $T$  and  $T_t$ ,  $T_t$  being the triple point of water (Fig. 6.2a), arbitrarily assigned the value 273.16 K,

$$\frac{Q_1}{Q_2} = \frac{T}{T_t}$$

$$T = 273.16 \frac{Q_1}{Q_2} \quad (\text{---})$$

If this equation is compared with the equation given ~~in article 6.2~~, it is seen that in the kelvin scale,  $Q$  plays the role of thermometric property. The amount of heat supplied  $Q$  changes with change in temperature just like the thermal emf in a thermopile.

(iii) That the absolute thermodynamic temperature scale has a definite zero point can be shown by imagining a series of reversible engines, extending from a source at  $T_1$  to lower temperature (Fig. 6)

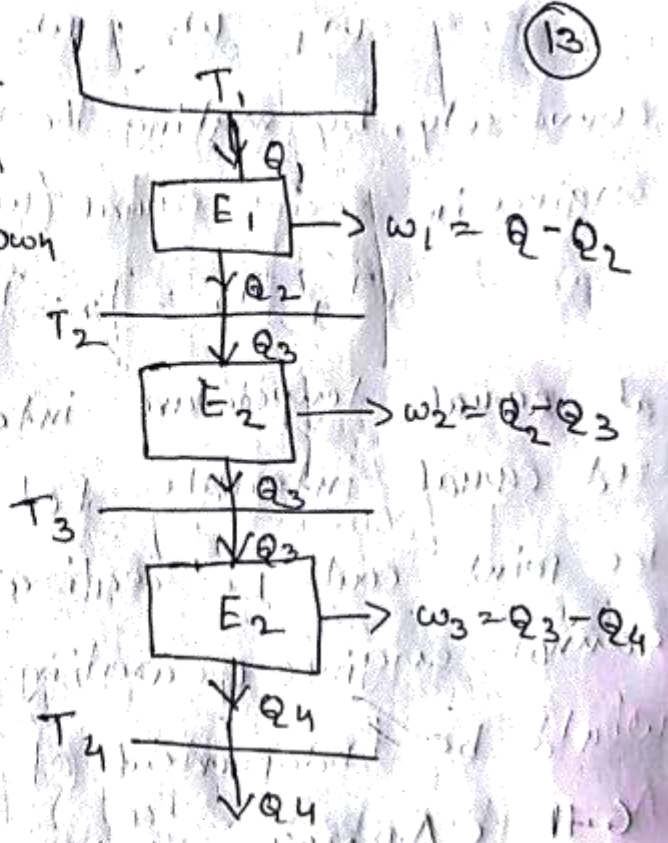


Fig. 6 Heat Engines operating in Series.

Since

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

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

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

or  $T_1 - T_2 = (Q_1 - Q_2) \frac{T_2}{Q_2}$

similarly  $T_2 - T_3 = (Q_2 - Q_3) \frac{T_3}{Q_3}$

$$= (Q_2 - Q_3) \frac{T_2}{Q_2}$$

$$T_3 - T_4 = (Q_3 - Q_4) \frac{T_2}{Q_2}$$

and so on

if  $T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \dots$ , assuming equal temperature intervals or  $Q_1 - Q_2 = Q_2 - Q_3 = Q_3 - Q_4 = \dots$

$w_1 = w_2 = w_3 = \dots$

conversely, by making the work quantities performed by the engines in series equal ( $w_1 = w_2 = w_3 = \dots$ ), we will get

$T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \dots$

at equal temperature intervals. A scale having one hundred equal intervals between the steam point and the ice point could be realized by a series of one hundred Carnot engines operating as in Fig 6.30. Such a scale would be independent of the working substance.

CARNOT CYCLE

A reversible cycle is an ideal hypothetical cycle in which all the processes constituting the cycle are reversible. Carnot is a reversible cycle. For a stationary system, as in a piston and cylinder machine, the cycle consists of the following four successive processes (Fig-6.30);

(a) A reversible isothermal process in which heat  $Q_1$  enters the system at  $t_1$  reversibly from a constant temperature source at  $t_1$ , when the cylinder cover is in contact with the diathermic cover A. The internal energy of the system increases.

From the First Law  $Q_1 = U_2 - U_1 + w_{1-2}$   
(for an ideal gas only,  $U_1 = U_2$ )

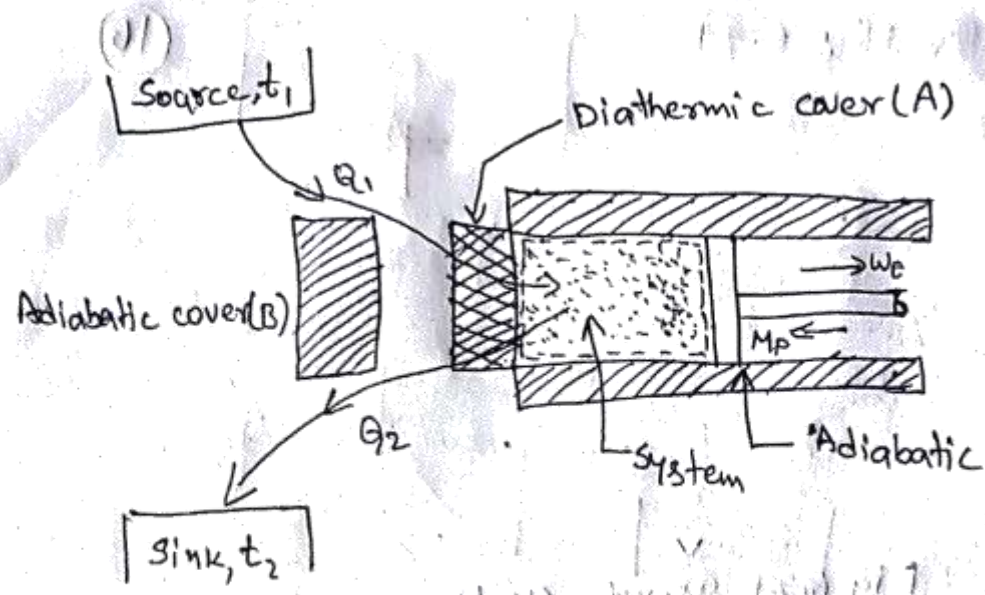


Fig. ~~1.2~~ Carnot Heat Engine - stationary system.

(b) A reversible adiabatic process in which the diathermic cover A is replaced by the Adiabatic cover B, and work  $W_E$  is done by the system adiabatically and reversibly at the expense of its internal energy, and the temperature of the system decreases from  $t_1$  to  $t_2$  using the first Law

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

(c) A reversible isothermal process in which B is replaced by A and heat  $Q_2$  leaves the system at  $t_2$  to a constant temperature sink at  $t_2$  reversibly, and the internal energy of the system further decreases.

From the first Law,  $-Q_2 = U_4 - U_3 - W_{3-4}$

$$U_3 = U_4$$

only for an ideal gas,

(d) A reversible adiabatic process in which B again replaces A, and work  $W_P$  is done upon the system reversibly, and adiabatically, and the internal energy of the system increases and the temperature rises from  $t_2$  to  $t_1$ .

Applying the first law

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

Two reversible isotherms and two reversible adiabatics constitute a Carnot cycle which is represented in P-V

(21) coordinates in Fig ~~6.11~~

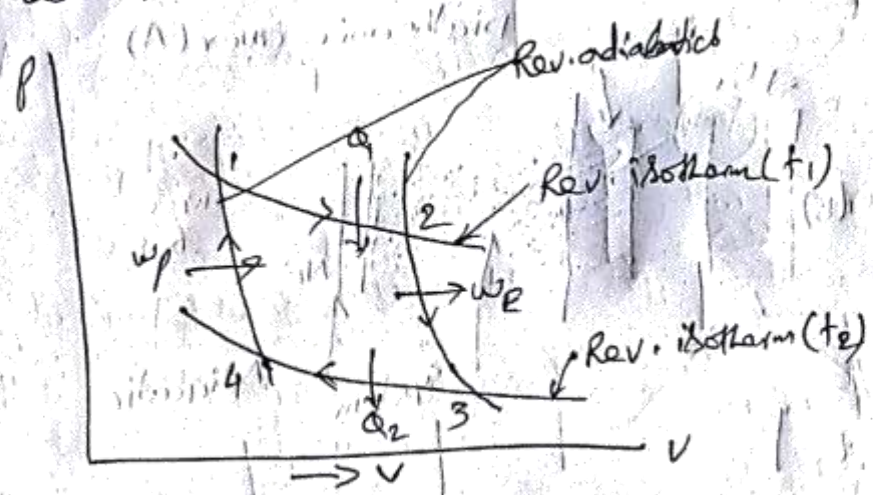


Fig ~~6.11~~ Carnot cycle

Summing up Eqs. (6.14) to (6.17),

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

or

$$\sum_{\text{cycle}} Q_{\text{net}} = \sum_{\text{cycle}} w_{\text{net}}$$

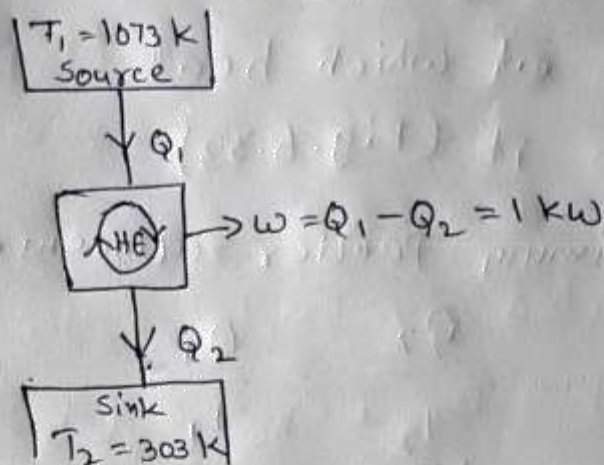
A cyclic heat engine operating on the Carnot cycle, is called a Carnot heat engine.

For a steady flow system, the Carnot cycle is represented as shown in Fig. ~~6.11~~. Here, heat  $Q_1$  is transferred to the system reversibly and isothermally at  $t_1$  in the heat exchanger (A), work  $w_T$  is done by the system reversibly and adiabatically in the turbine (B), then heat  $Q_2$  is transferred from the system reversibly and isothermally at  $t_2$  in the heat exchanger (C) and then work  $w_p$  is done upon the system reversibly and adiabatically by the pump (D). To satisfy the conditions for the Carnot cycle, there must not be any friction or heat transfer in the pipelines through which the working fluid flows.



Example 6.1 A cyclic heat engine operates between a source temperature of  $800^{\circ}\text{C}$  and a sink temperature of  $30^{\circ}\text{C}$ . What is the least rate of heat rejection per kW net output of the engine?

Solution For a reversible engine, the rate of heat rejection will be minimum (Fig. ~~6.1~~)

Fig. ~~6.1~~

$$\eta_{\text{max}} = \eta_{\text{rev}} = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{30 + 273}{800 + 273}$$

$$= 1 - 0.282 = 0.718$$

$$\frac{w_{\text{net}}}{Q_1} = \eta_{\text{max}} = 0.718$$

$$Q_1 = \frac{1}{0.718} = 1.392 \text{ kW}$$

$$Q_2 = Q_1 - w_{\text{net}} = 1.392 - 1 = 0.392 \text{ kW}$$

This is the least rate of heat rejection.

Example 6.2 A domestic food freezer maintaining a temperature of  $-15^{\circ}\text{C}$  the ambient air temperature is  $30^{\circ}\text{C}$ . If heat leaks into the freezer at the continuous rate of  $1.75 \text{ kJ/s}$  what is the least power necessary to pump this heat out continuously?

(Solution Freezer temperature

$$T_2 = -15 + 273 = 258 \text{ K}$$

Ambient air temperature

$$T_1 = 30 + 273 = 303 \text{ K}$$

The refrigerator cycle removes heat from the freezer at the same rate at which heat leaks into it (Fig. 6.33)

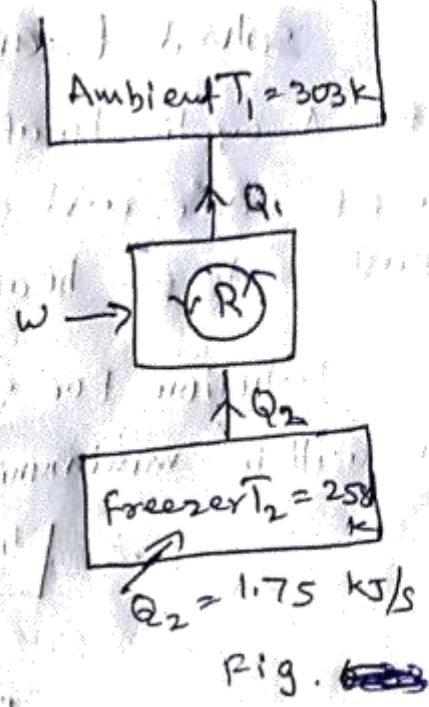


Fig. 6.33

For minimum power requirement

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

$$\therefore Q_1 = \frac{1.75}{258} \times 303 = 2.06 \text{ kJ/s}$$

$$\therefore W = Q_1 - Q_2 = 2.06 - 1.75 = 0.31 \text{ kJ/s} = 0.31 \text{ kW}$$

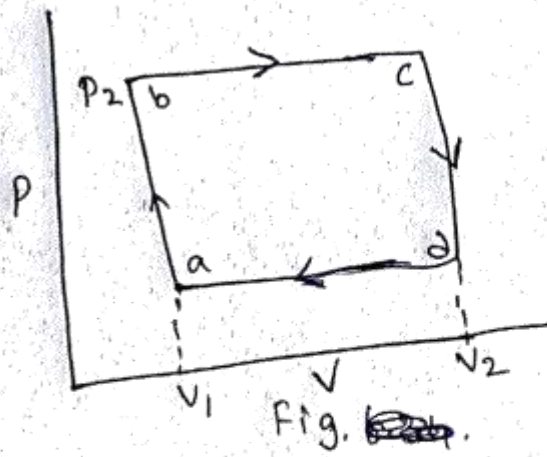
Example 6.3 An ideal gas cycle is represented by a rectangle on a p-v diagram. If  $p_1$  and  $p_2$  are the lower and higher pressures; and  $v_1$  and  $v_2$  the smaller and larger volumes, respectively then (a) calculate the work done per cycle, (b) indicate which parts of the cycle involve heat flow into the gas, (c) show that

$$\eta = \frac{\gamma - 1}{\gamma \frac{p_2}{p_1} + \frac{v_1}{v_2 - v_1}}$$

if heat capacities are constant.

Solution

19



(a)  $w = \text{area of the cycle (Fig. 6.34)}$   
 $= (P_2 - P_1)(V_2 - V_1)$  Ans.

(b) processes ab and bc

Heat absorbed by 1 mole of gas in one cycle

$$Q = Q_{ab} + Q_{bc} = C_v(T_b - T_a) + C_p(T_c - T_b)$$

Now,  $T_a = T_b \frac{P_1}{P_2}$  and  $V_1 = R T_b$

$$T_c = T_b \frac{V_2}{V_1}, T_b = \frac{P_2 V_1}{R}$$

$$Q = C_v T_b \left[ 1 - \frac{P_1}{P_2} \right] + C_p T_b \left[ \frac{V_2}{V_1} - 1 \right]$$

$$= \frac{P_2 V_1}{R} \left[ C_p \frac{P_2 - P_1}{P_2} + C_p \frac{V_2 - V_1}{V_1} \right] \text{ Ans.}$$

# (5) Thermodynamic Relations ①

Fundamentals of partial differentiation :- If three variables are represented by  $x, y, z$ . Their functional relationship may be expressed in the following form

$$f(x, y, z) = 0$$

$$x = x(y, z)$$

$$y = y(x, z)$$

$$z = z(x, y)$$

Let  $x$  is a function of two independent variables  $y$  and  $z$

$$x = x(y, z)$$

Then the differential of the dependent variable  $x$  is given by

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad \text{--- (1)}$$

$$dx = M dy + N dz \quad \text{--- (2)}$$

partial differentiation of  $M$  and  $N$

w.r.t.  $z$  and  $y$ , respectively, gives

$$M = \left(\frac{\partial x}{\partial y}\right)_z$$

$$N = \left(\frac{\partial x}{\partial z}\right)_y$$

$$\frac{\partial M}{\partial z} = \frac{\partial^2 x}{\partial y \partial z}$$

$$\frac{\partial N}{\partial y} = \frac{\partial^2 x}{\partial y \partial z}$$

$$\therefore \frac{\partial M}{\partial z} = \frac{\partial N}{\partial y} \quad \text{--- (4)}$$

$dx$  is a perfect differential when Eqn (4) is satisfied for any function of  $x$ .

where  $dx$  is called an exact differential

$$\text{If } \left(\frac{\partial x}{\partial y}\right)_z = M$$

$$\left(\frac{\partial x}{\partial z}\right)_y = N$$

Similarly if  $y = y(x, z)$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$z = z(x, y)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x \left[ \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \right]$$

$$= \left[ \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \right] dx + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$= \left[ \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \right] dx + dy$$

$$\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = 0$$

$$\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = - \left(\frac{\partial y}{\partial x}\right)_z$$

$$\therefore \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

In terms of  $p, v, T$ , the following relation holds good

$$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial v}{\partial T}\right)_p = -1$$

General Thermodynamic Relations

The first law applied to a closed system undergoing a reversible process states that

$$dq = du + pdv$$

$$Tds = du + pdv \quad ds = \left(\frac{dq}{T}\right)_{rev}$$

$$du = Tds - pdv \quad \text{--- (1)}$$

Enthalpy is given by

$$h = u + pv$$

$$dh = du + d(pv)$$

$$= du + pdv + vdp$$

$$= Tds - pdv + pdv + vdp \quad (\text{from eqn (1)})$$

$$dh = Tds + vdp \quad \text{--- (2)}$$

Gibbs function is given by

$$g = h - TS$$

$$dg = dh - d(TS)$$

$$= dh - Tds - SdT$$

$$= Tds + vdp - Tds - SdT \quad (\text{from eqn (2)})$$

$$= vdp - SdT \quad \text{--- (3)}$$

Helmholtz function is given by

$$f = u - TS$$

$$df = du - d(TS) = du - Tds - SdT$$

$$= Tds - pdv - Tds - SdT \quad (\text{from (1)})$$

$$df = -pdv - SdT \quad \text{--- (4)}$$

internal energy, enthalpy, Gibbs function, Helmholtz (5)

function and properties then  $du$ ,  $dh$ ,  $dg$ ,  $df$  are exact differentials.

$\therefore$  Apply the test for exactness

If  $dx = Mdy + Ndz$

$x = x(y, z)$

$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$

$dx = Mdy + Ndz$

If  $dz = Mdx + Ndy$  is a property, then

$z = z(x, y)$

$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

$dz = Mdx + Ndy$

$M = \left(\frac{\partial z}{\partial x}\right)_y$

$N = \left(\frac{\partial z}{\partial y}\right)_x$

$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$ ,  $\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$

$\therefore \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

Consider Eqn (1),  $du = Tds - pdv$   
 $dz = Mdx + Ndy$

$M = T$

$x = S$

$N = -p$

$y = v$

$\therefore \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$  (5)

Consider Eqn (2),  $dh = Tds + v \cdot dp$   
 $dz = Mdx + Ndy$

$M = T$

$x = S$

$N = v$

$y = p$

$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$  (6)

Consider Eqn (3),  $dg = v dp - s dT$

Compare with  $dz = M dx + N dy$

$M = v$   
 $x = p$   
 $N = -s$   
 $y = T$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \quad \text{--- (7)}$$

Consider Eqn (4),  $df = -p dv - s dT$   
 $dz = M dx + N dy$

$M = -p$   
 $x = v$   
 $N = -s$   
 $y = T$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$-\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad \text{--- (8)}$$

Rewrite the eqns (5), (6), (7) & (8) are

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

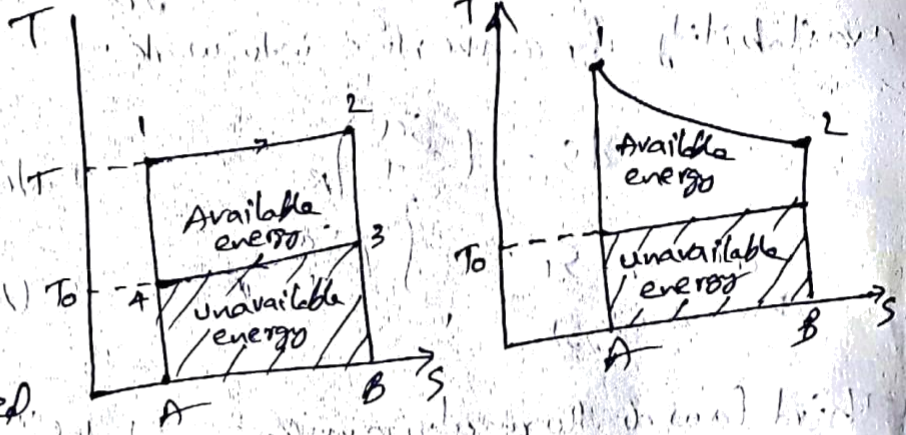
} These four equations are known as Maxwell's relations and are used to determine relationship between the properties  $p, v, T,$  and  $s$  for any equilibrium state.



Clausius inequality, Entropy, principle of entropy increase, Energy equation, availability and irreversibility - Thermodynamic potentials, Gibbs and Helmholtz functions, Maxwell relations, Elementary treatment of the third law of thermodynamics.

Available energy

It is not possible to convert all the heat absorbed by a system into work.



If  $Q_1$  heat is absorbed

$W$  by the engine (say  $Q_1 = 70 \text{ kJ}$ ).

only some heat is utilized to convert ~~to~~ work and ~~the~~ some heat is rejected to atmosphere.

$Q_1 = AE + UE$   
 $W_{max} = AE = Q_1 - AE$

If  $Q_1 = 70 \text{ kJ}$ ,  $W = 50 \text{ kJ}$  then  $Q_2 = 20 \text{ kJ}$  rejects to atmosphere.

Therefore  $50 \text{ kJ}$  is the available energy and  $20 \text{ kJ}$  is the unavailable energy.

The area 1-2-3-4 represents the available energy.

The shaded area A-3-B-A represents the energy, which is discarded to the ambient atmosphere, and this quantity of energy cannot be converted into work and is called unavailable energy.

Irreversibility: - The actual work which a system does is always less than the idealized reversible work, and the difference between the two is called the irreversibility of the process.

Thus, Irreversibility,  $I = W_{max} - W$

This is also sometimes referred to as 'degradation' or 'dissipation'.

Available energy → is the maximum portion of energy which could be converted into useful work is known as available energy.

Entropy :- is a function of a quantity of heat which shows the possibility of conversion of that heat into work. The increase in entropy is small when heat is added at a high temperature and is greater when heat addition is made at lower temperature. Thus for maximum entropy, there is a minimum availability for conversion into work and for minimum entropy there is maximum availability for conversion into work.

$$ds = \left( \frac{\delta Q}{T} \right)_R$$

Entropy change,  $ds = \frac{\text{Heat change } (Q)}{\text{Absolute temperature } (T)}$

$$\text{or } S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right)_R$$

Unit  $\rightarrow S = \frac{J}{K} = J/K$

(change of entropy)

Third law of thermodynamics states "when a system is at zero absolute temperature, the entropy of system is zero".

(or)

"The entropy of all perfect crystalline solids is zero at absolute zero temperature".

Entropy  $\rightarrow$  May also be defined as the thermal property of a substance which remains constant when substance is expanded or compressed adiabatically in a cylinder.

Thermal Energy Reservoir (TER):-

- It is defined as a large body of infinite heat capacity, which is capable of absorbing or rejecting an unlimited quantity of heat without suffering the considerable changes in its thermodynamic coordinates. It is simply called "Reservoir."

(or)

- It is a body with a relatively large thermal capacity that can supply or absorb finite amount of heat without any change in temperature.

Eg: large bodies of water such as oceans, lake, Rivers, atmosphere

Source:- It is a Thermal Energy Reservoir/Reservoir that supplies energy in the form of heat. ~~is~~

Source

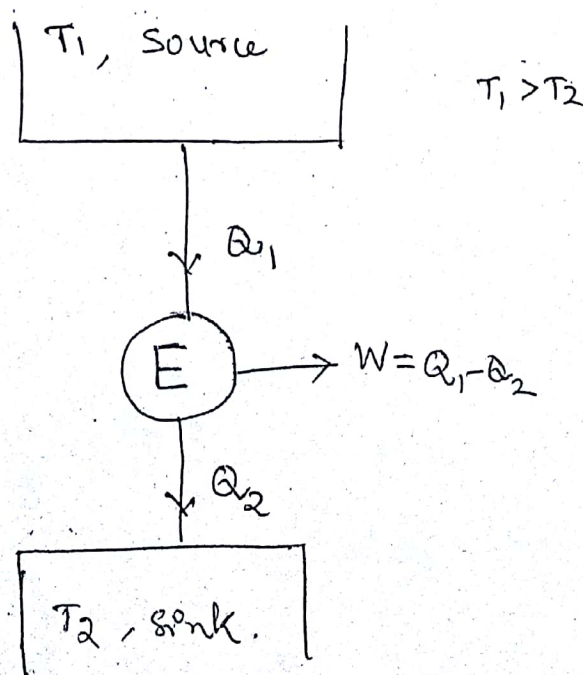
Sink: It is a TER that absorbs energy in the form of Heat.

(2)

## Heat engines:-

→ Work can be converted into ~~work~~ Heat completely <sup>The</sup> and directly, but converting Heat into work requires the use of special Devices, called "Heat Engines".

- (1) They receive the Heat from a high-temperature source
- (2) They convert only part of heat to work (usually in the form of shaft work)
- (3) They reject the remaining waste heat to a - Low temperature sink.
- (4) They operate on a cycle.



Notes

- ③
- The Heat engine Receives the Heat  $Q_1$  from Source at a temperature of  $T_1$ ,
  - Rejecting Heat  $Q_2$  to a sink at temperature  $T_2$ ,
  - Producing a Net work output of "W".

→ Efficiency ( $\eta$ ) =  $\frac{\text{work output}}{\text{Heat supply}}$

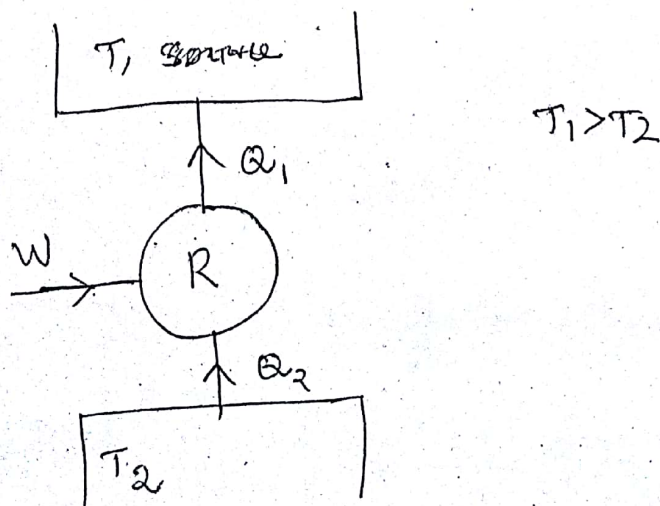
\*  $\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$

\*  $\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$

→ The value of ' $\eta$ ' is ' $< 1$ '  $\therefore \eta < 1$   
→ ' $\eta$ ' value lies between (0 and 1)

Refrigerator :-

The Transfer of heat from a low temperature medium to a high temperature medium requires a special Device called "Refrigerator".



④ → By the virtue of input work ( $W$ ), Heat can travel from low temperature body <sup>Heat</sup> sink at temperature ( $T_2$ ) to a high temperature source at temperature ( $T_1$ ).

→ The efficiency of 'Refrigerator' is expressed in terms of "COP".

- Coefficient of performance (COP) =  $\frac{\text{Heat Rejection}}{\text{Work input}}$

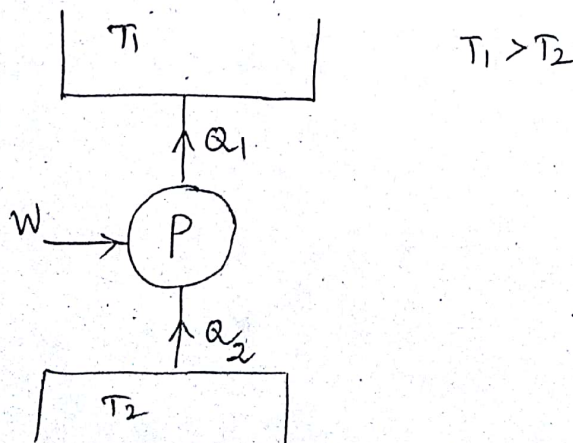
\*  $\therefore$  COP =  $\frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$

\* COP =  $\frac{T_2}{T_1 - T_2}$

→ Refrigerator maintaining a body temperature lower than the surroundings.

Heat pump :-

→ Heat pump is a device which operates in a cycle maintaining a body temperature higher than the surroundings.



(5)

$$W + Q_2 = Q_1$$

$$W = Q_1 - Q_2$$

→ COP is the performance parameter for heat pump

$$\rightarrow * COP = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2}$$

$$* COP = \frac{T_1}{T_1 - T_2}$$

→ Relation between COP of Refrigerator & Heat pump,

$$\begin{aligned} (COP)_{\text{Ref}} &= \frac{Q_2}{Q_1 - Q_2} \\ &= \frac{Q_2 + (Q_1 - Q_1)}{Q_1 - Q_2} = \frac{Q_1}{Q_1 - Q_2} + \frac{Q_2 - Q_1}{Q_1 - Q_2} \\ &= \frac{Q_1}{Q_1 - Q_2} - \left( \frac{Q_1 - Q_2}{Q_1 - Q_2} \right) \end{aligned}$$

$$(COP)_{\text{Ref}} = (COP)_{\text{pump}} - 1$$

$$\checkmark * \therefore (COP)_{\text{pump}} = (COP)_{\text{Ref}} + 1$$

→ C.O.P is always greater than 1.

$$* COP > 1$$

(6)

## Second Law of Thermodynamics (1D-2):-

→ The second law of thermodynamics is explained by two statements. (i) kelvin-planck statement, (ii) clausius statement.

### (i) kelvin-planck's statement of second law:-

"It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single fixed temperature."

$$\eta_{\text{engine}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} < 1$$

$$\therefore 1 - \frac{Q_2}{Q_1} < 1$$

$$\Rightarrow \frac{Q_2}{Q_1} > 0$$

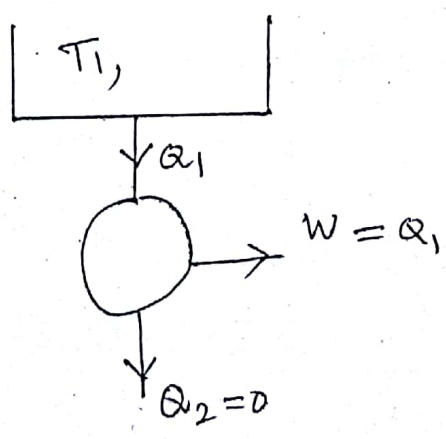
$$\Rightarrow Q_2 > 0$$

i.e. to produce net work in a cycle; the engine has exchange heat with two reservoirs, (two different temperatures) called source, sink.



→ if  $Q_2 = 0$ ; the engine will produce net work in a cycle by exchanging heat only with one reservoir, thus violating the Kelvin-Planck statement. Such an engine is called a perpetual motion machine of second kind, PMM-2. A PMM-2 is impossible.

"It is impossible for a heat engine which works on cycle by exchanging heat at single temperature source". It is PMM-2.



(ii) Clausius statement of second law:-

"It states that, "It is impossible to construct a device which, operating in a cycle, will produce no effect other than transfer of heat from cooler to hotter body".

8

→ Heat cannot flow itself from a body at low temperature to a body at higher temperature. Some work must be spend to achieve it.

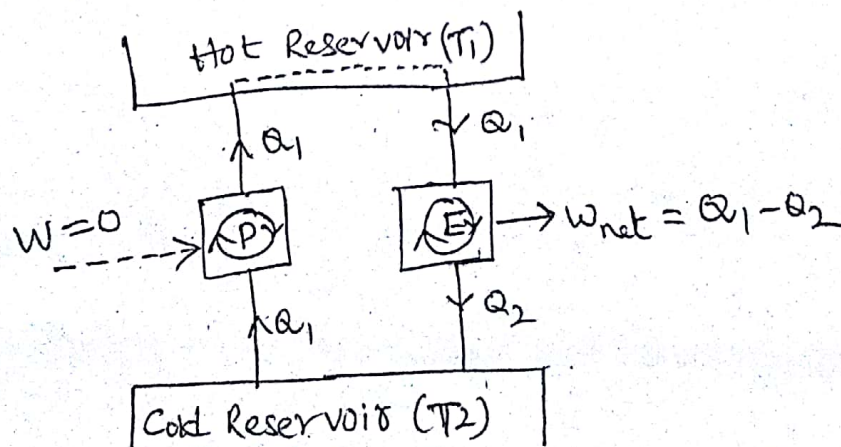
we assume between the two...

### Equivalence of Kelvin-Planck and Clausius statements:-

The equivalence of Kelvin-Planck & Clausius statements will be proved if it can be shown that the violation of one statement implies the violation of second statement and vice versa.

#### (a) violation of Clausius statement:-

Let us first consider a cyclic heat pump  $P'$  which ~~does~~ transfers heat from a low temperature reservoir ( $T_2$ ) to a high temperature reservoir ( $T_1$ ) with no other effect, i.e. with no expenditure of work, thus violating Clausius statement.



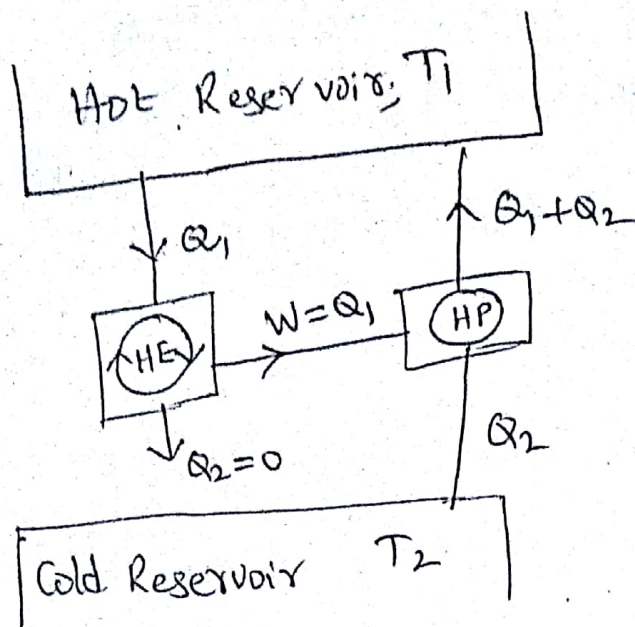
(9)

Let us assume a cyclic heat Engine 'E' operating between the same thermal energy reservoirs, producing  $W$  net in one cycle. The rate of working of heat engine is such that it draws an amount of heat ' $Q_1$ ' from the hot reservoir equal to discharged by the heat pump. Then the hot reservoir is may be eliminated that heat ' $Q_1$ ' is discharged by pump is fed to heat engine. So heat pump 'P' and engine 'E' acting together constitute a heat engine operating in a cycle producing only net work as heat at a single fixed temperature.

(b) Violation of Kelvin-Planck statement:-

Let us consider a PMM-2, which produces net work in a cycle by exchanging heat only with one thermal reservoir at  $T_1$ , and thus violates the Kelvin-Planck statement.

(10)



Process 1: 1  
 Process 2: 2  
 Process 3: 3

Let us assume, a cyclic heat pump (P) extracting heat  $Q_2$  from  $T_2$ , and discharging heat to a high temperature  $T_1$ , with expenditure of work "W" equal to what the PPM2 delivers in a complete cycle. So E & P together constitute a heat pump working in a cycle and producing the sole effect of transferring heat from a lower to a higher temperature body, thus violating Clausius statement.

### \* Carnot Cycle:-

→ Carnot cycle is a Reversible cycle.

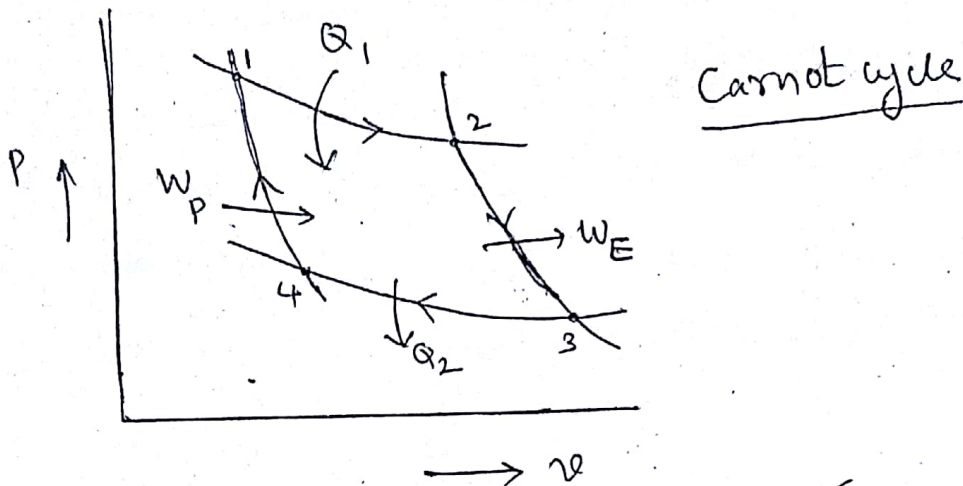
→ It consists of Four Reversible processes.

Process 1 :  $1 \rightarrow 2$ : Reversible Isothermal Heat addition.  
( $Q_1$ )

Process 2 :  $2 \rightarrow 3$ : Reversible Adiabatic work output [exp] [ansim]  
( $W_E$ )

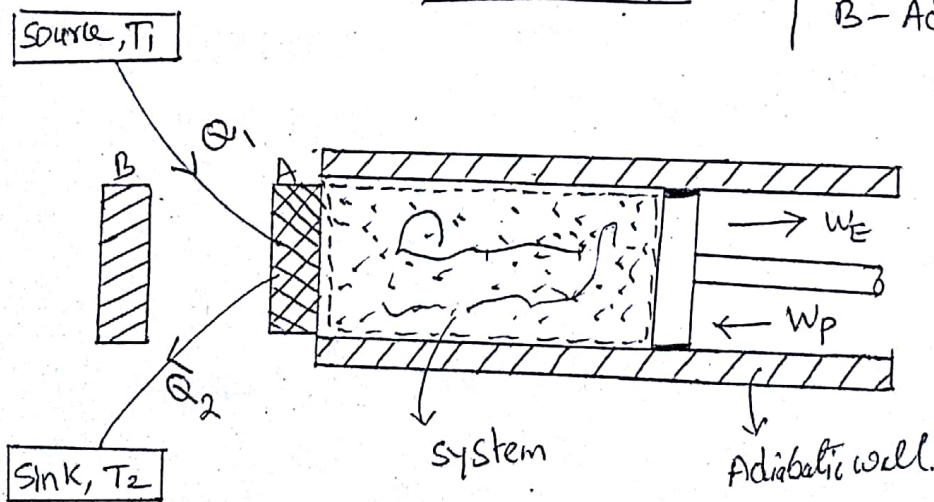
Process 3 :  $3 \rightarrow 4$ : Reversible Isothermal Heat Rejection.  
( $Q_2$ )

Process 4 :  $4 \rightarrow 1$ : Reversible Adiabatic work input [compression]  
( $W_P$ )



→ A cyclic Heat engine works on Carnot cycle is called "Carnot engine"

A - Diathermic wall  
B - Adiabatic wall.



Carnot Engine

(12)

Process 1: (1 → 2): It is Reversible Isothermal in which heat  $Q_1$  enters the system at  $T_1$ . when cylinder cover is contact with a diathermic wall (A). The Internal Energy of system Increases.

$$\text{From TD-1: } Q_1 = (U_2 - U_1) + W_{1-2} \quad \text{--- (a)}$$

Process 2: (2 → 3): It is a Reversible Adiabatic expansion, in which cover 'A' is replaced by a Adiabatic Cover B, and  $W_E$  is work done by the system. The Internal Energy of the system decreases

$$\text{From TD-1: } 0 = (U_3 - U_2) + W_{2-3} \quad \text{--- (b)}$$

Process 3: (3 → 4): It is Reversible Isothermal heat rejection process. in which cover 'B' is replaced by 'A'. and Heat  $Q_2$  leaves to sink at  $T_2$ . The Internal Energy of the system decreases.

$$\text{From TD-1: } -Q_2 = (U_4 - U_3) - W_{3-4} \quad \text{--- (c)}$$

Process 4: (4 → 1): It is a reversible Adiabatic Compression process. The Cover 'B' is replaced by 'A'. and work  $W_P$  is done upon the system. The Internal Energy is Increases.

$$\text{From TD-1: } 0 = (U_1 - U_4) - W_{4-1} \quad \text{--- (d)}$$

work

Summing the eq's a, b, c, d ( $\therefore (a) + (b) + (c) - (d)$ ) <sup>(12)</sup>

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

$$\therefore \sum_{\text{cycle}} Q_{\text{net}} = \sum_{\text{cycle}} W$$

→ Carnot cycle is an ideal cycle (b) Carnot engine is ideal engine/Reference engine.

→ No body can create a Carnot engine

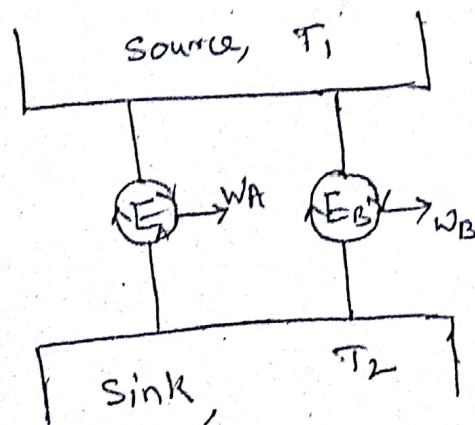
$$\therefore \eta = \text{efficiency} = 1 - \frac{T_L}{T_H} = 1 - \frac{T_2}{T_1}$$

$T_L =$  Lower temperature of cycle  $= T_2$

$T_H =$  Higher temperature of cycle  $= T_1$

Carnot theorem:

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



(14) Absolute Thermodynamic Temperature Scale:-

Let us consider  
 $E_1, E_2$  etc.

The efficiency of heat engine cycle is given by

$$\eta = \frac{W_{net}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad \text{--- (a)}$$

- by TD-2, The temperature difference ( $T_1 - T_2$ ) is required for work done.

- We know, (from Carnot theory), the efficiency of all heat engines operating between the same temperature levels is same. i.e. efficiency will depend solely on temperatures  $T_1, T_2$ .

$$\eta_{rev} = f(T_1, T_2) \quad \text{--- (b)} \quad \text{f - function of temperature}$$

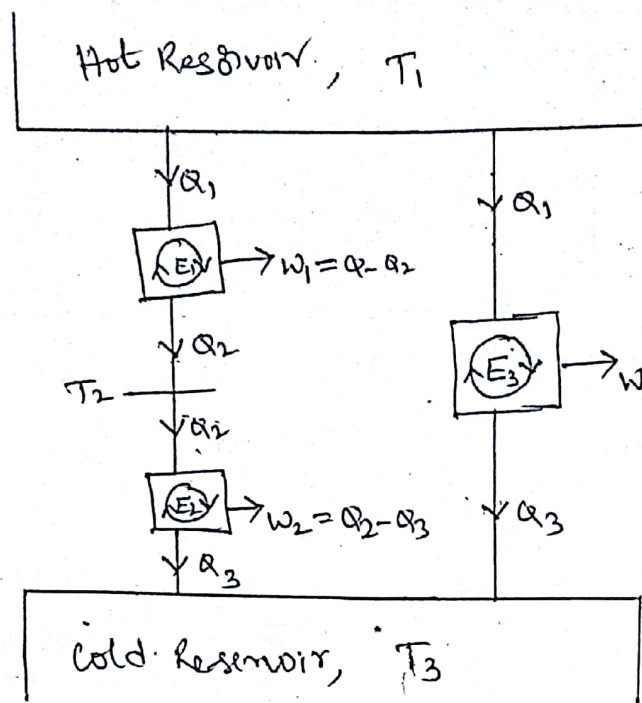
- From (a), (b)  $\Rightarrow 1 - \frac{Q_2}{Q_1} = f(T_1, T_2)$

$$\Rightarrow \frac{Q_1}{Q_2} = F(T_1, T_2); \quad T - \text{New function.}$$

- If some functional relationship exists between  $T_1, T_2$ , and  $Q_1/Q_2$  then the equation becomes the Definition of temperature scale.



→ Let us consider two reversible heat engines  $E_1, E_2$  operating  $T_1, T_2$ ; &  $T_2, T_3$ ;



- Now  $\frac{Q_1}{Q_2} = F(T_1, T_2)$ ;  $\frac{Q_2}{Q_3} = F(T_2, T_3)$

- Now  $E_1, E_2$  together constitute a another Heat engine  $E_3$  operating between  $T_1$  &  $T_3$ .

$$\therefore \frac{Q_1}{Q_3} = F(T_1, T_3)$$

$$\therefore \frac{Q_1}{Q_2} = \frac{Q_1/Q_3}{Q_2/Q_3} = \frac{F(T_1, T_3)}{F(T_2, T_3)}$$

$$\frac{Q_1}{Q_2} = F(T_1, T_2) = \frac{F(T_1, T_3)}{F(T_2, T_3)} \quad \text{--- (C)}$$

(16)

→ So, ' $T_3$ ' will drop out from the ratio in  $\dots$   
→ after  $T_3$  has been cancelled, the Numerator  $\rightarrow$  when second  $\rightarrow$   
is written  $\phi(T_1)$ ; denominator as  $\phi(T_2)$ .  $\rightarrow$  to definition of

$$\therefore \frac{Q_1}{Q_2} = F(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} ; \phi - \text{unknown fn}$$

→ Kelvin proposed that ;  $\phi(T_1) = T_1$   
 $\phi(T_2) = T_2$

$$\therefore \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{Absolute temperature scale.}$$

→ The Absolute Thermodynamic temperature scale  
is known as Kelvin-scale.

# Entropy

(17)

→ When second law applied to process, it leads to definition of new property, known as "Entropy".

## Clausius theorem :-

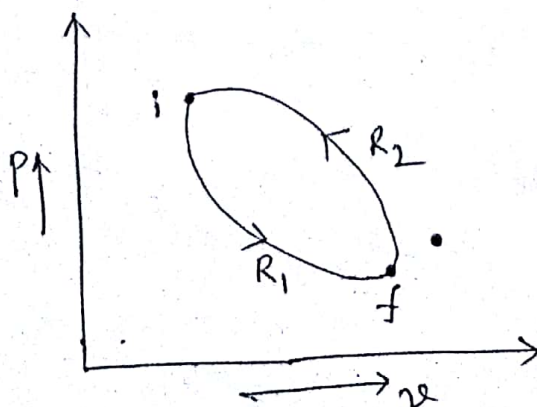
"The cyclic integral of  $dQ/T$  for a Reversible cycle is equal to zero".

$$\oint_R \frac{dQ}{T} = 0 \quad ; \quad R - \text{Reversible.}$$

## Entropy :-

Let a system be taken from initial equilibrium  $i$  to final equilibrium  $f$  by a path  $R_1$ . The system is brought back from  $f$  to  $i$  following another reversible path  $R_2$ . Now the two paths  $R_1$  and  $R_2$  together form a reversible cycle.

From Clausius theorem;  $\oint_{R_1, R_2} \frac{dQ}{T} = 0$



$R_1: i \rightarrow f$   
 $R_2: f \rightarrow i$

(18) → The above integral may be written as

$$\oint_{R_1}^f \frac{dq}{T} + \oint_{fR}^i \frac{dq}{T} = 0$$

$$\Rightarrow \int_{R_1}^f \frac{dq}{T} = - \int_{R_2}^i \frac{dq}{T}$$

$$\Rightarrow \int_{R_1}^f \frac{dq}{T} = \int_{R_2}^f \frac{dq}{T}$$

∴ So,  $\int_i^f \frac{dq}{T}$  is independent of the reversible path connecting  $i \rightarrow f$ . Therefore, there exists a property

of a system, whose value at the final state  $f$  minus its value at  $i$  is equal to  $\int_i^f \frac{dq}{T}$ .

This property is called "Entropy". It is denoted by "s". " $s_i$ " denotes the entropy at initial state and " $s_f$ " denotes the entropy at final state.

$$\therefore \int_{R_1}^f \frac{dq}{T} = s_f - s_i = ds$$

→ Entropy (s) is a point function; and is a property.

→ Its units are " $J/kg \cdot K$ ".

## inequality of Clausius :-

(19)

$$\oint \frac{dq}{T} \leq 0$$

The equation is known as Clausius inequality. It provides the criterion of the Reversible cycle.

\*  $\oint \frac{dq}{T} = 0$ , Reversible cycle

\*  $\oint \frac{dq}{T} < 0$ , Irreversible cycle, possible

\*  $\oint \frac{dq}{T} > 0$ , cycle is impossible, it violates the second law.

## Entropy for process :-

$$\oint \frac{dq}{T} = ds = 0; \text{ Reversible process}$$

$\oint$

→  $ds = \frac{dq}{T} = 0$ ; Reversible process

→  $ds > 0$ ;  $ds < 0$ ; irreversible process

# Entropy principle:-

For an infinitesimal process undergone by a system

$$ds \geq \frac{dq}{T}$$

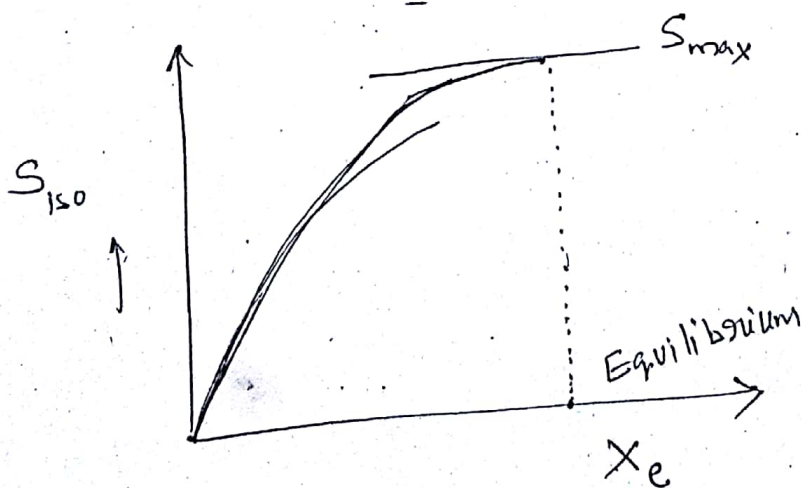
For a Isolated system,  $dQ = 0$  (Heat Transfer is zero)

$$\therefore ds_{iso} \geq 0$$

but for a Reversible process  $ds = 0 \Rightarrow \frac{dq}{T} = 0$

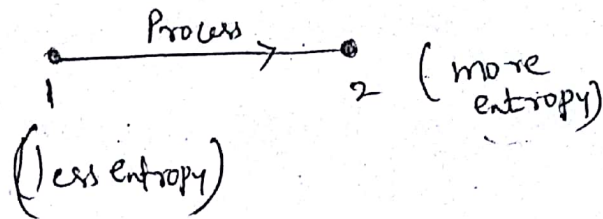
$$\Rightarrow S = \text{Constant.}$$

$\therefore$  i.e. The entropy of isolated system can never decrease, It always increases and remains constant only when the process is reversible. This is the principle of increase of entropy.



## General expressions for entropy change:-

(21)



$$s_2 - s_1 = ds = C_v \ln\left(\frac{P_2}{P_1}\right) + C_p \ln\left(\frac{V_2}{V_1}\right)$$

$$s_2 - s_1 = ds = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$

$$s_2 - s_1 = ds = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$$

### Some Facts about Entropy:-

→ Entropy of an isolated system can never decrease

→ only possible processes in nature that cause the increase of Entropy.

→ All the spontaneous processes in nature occur only in one direction from higher potential to a lower potential, and these are accompanied by an entropy increase of universe.

→ Any process occurs in such a direction as to cause an increase in the entropy of universe.

(12)

→ The Second Law of Thermodynamics indicates the direction in which process takes place.

→ Entropy is nothing but degree of disorder.

→ Any irreversible process always tends to increase of disorder.

→ So there is a close link between Entropy and disorder.

i.e. Entropy of a system is a measure of degree of molecular disorder existing in the system.



## Available energy (Exergy)

→ The sources of energy can be divided into two groups

(i) High grade energy      (ii) Low grade energy

→ Mechanical work

→ Electrical work

→ Windpower

→ Tidal power

→ Kinetic Energy etc.

→ Heat / Thermal energy

→ Heat from Nuclear fission, or fission

→ Heat from combustion of fossil fuel.

→ The complete ~~conservation~~ <sup>conversion</sup> of Low grade energy heat into high grade energy is impossible by virtue of the second law of T.D.

→ The part of low grade energy available for conversion is referred as "Available Energy". While remaining part is rejected, it is known as "unavailable energy".

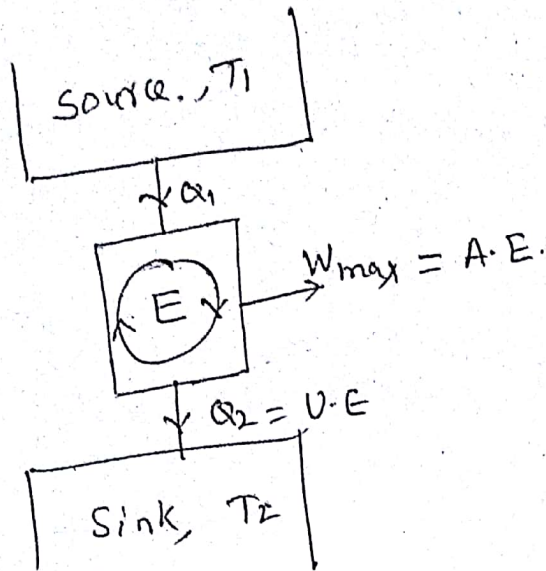
→ The maximum work output obtainable from a certain heat input in a cyclic heat engine is called the "available Energy".

24

A.E = Available Energy

(-)

U.E = Unavailable Energy



$$Q_1 = A.E + U.E$$

$$W_{max} = A.E = Q_1 - U.E$$

$$\eta_{rev} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = \frac{W_{max}}{Q_1}$$

$$\rightarrow \eta_{rev} = 1 - \frac{T_2}{T_1}$$

From above expression, for a given  $T_1$ ,  $\eta_{rev}$  will increase with decrease of  $T_2$ , i.e. The lowest temperature of heat rejection is the temperature of ~~source~~ surroundings,  $T_0$

$$\therefore \eta_{max} = 1 - \frac{T_0}{T_1} = \frac{W_{max}}{Q_1}$$

## Problems

Q) A cyclic heat engine operates b/w a source temperature of  $800^{\circ}\text{C}$  and a sink temperature of  $30^{\circ}\text{C}$ . What is the least rate of heat rejection per kW net output of the engine?

sol) Given that it is a cyclic heat engine i.e. Reversible Heat engine.

$$\eta_{\max} = 1 - \frac{T_2}{T_1}$$

$$T_1 = 800^{\circ}\text{C} = 800 + 273 = 1073 \text{ K}$$

$$T_2 = 30^{\circ}\text{C} = 30 + 273 = 303 \text{ K}$$

$$\eta_{\max} = 1 - \frac{303}{1073} = 0.718$$

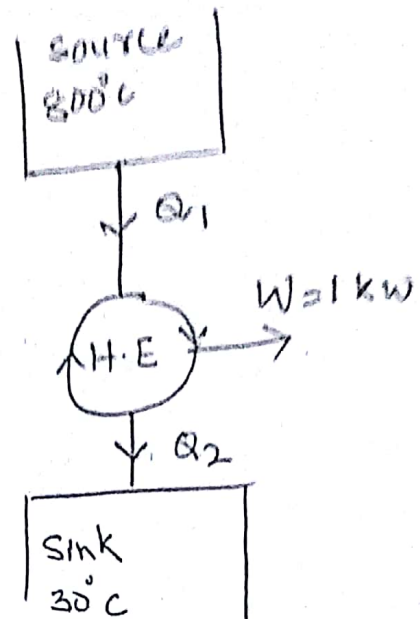
$$\eta_{\max} = \frac{W_{\text{net}}}{Q_1} = \frac{1}{Q_1} = 0.718$$

$$\Rightarrow Q_1 = 1.392 \text{ kW}$$

When H.E is Reversible  $Q_2$  will be minimum.

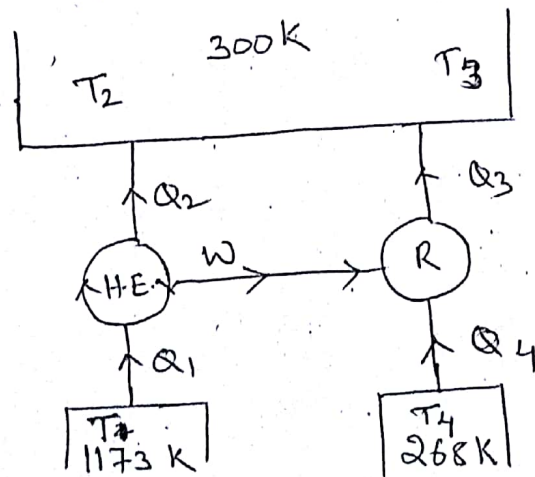
$$W_{\text{net}} = Q_1 - Q_2 = 1 \text{ kW}$$

$$\Rightarrow Q_2 = Q_1 - W_{\text{net}} = 1.392 - 1 = 0.392 \text{ kW}$$



② A Carnot heat engine receives heat from the Reservoir at  $1173\text{ K}$  at a rate of  $800\text{ kJ/min}$  and reject the waste heat to the ambient air at  $300\text{ K}$ . The entire work output of the heat engine is used to drive a refrigerator that removes heat from the refrigerated space at  $268\text{ K}$  and transfer it to the same ambient air at  $300\text{ K}$ . Determine the maximum rate of heat removal from the refrigerated space and total rate of heat rejection to the ambient air.

Sol) Given that it is a Carnot Heat engine, i.e. Reversible Heat engine.



$$Q_1 = 800\text{ kJ/min} = \frac{800\text{ kJ}}{60\text{ s}} = 13.34\text{ kW}$$

$$\therefore Q_1 = 13.34\text{ kW}$$

(3)

$$\eta_{\max} = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{1173} = 0.7442 = 74.42\%$$

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

$$\Rightarrow Q_2 = Q_1 (1 - \eta_{\max}) = 13.34 (1 - 0.7442)$$

$$Q_2 = 3.411 \text{ kW}$$

$$\therefore (W_{\text{net}})_{\text{HE}} = Q_1 - Q_2 = 13.34 - 3.411$$
$$(W_{\text{net}})_{\text{HE}} = 9.93 \text{ kW}$$

$$(\text{C.O.P})_{\text{Ref}} = \frac{Q_4}{(W_{\text{net}})_{\text{Ref}}} = \frac{Q_4}{(W_{\text{net}})_{\text{HE}}} = \frac{T_4}{T_3 - T_4}$$

$\therefore$  for maximum heat reject removal, Refrigerator should be Reversible,

$$\therefore (\text{C.O.P})_R = \frac{Q_4}{T_3 - T_4} = \frac{268}{300 - 268} = 8.375$$

$$\therefore (\text{COP})_R = 8.375 = \frac{Q_4}{Q_3 - Q_4} = \frac{Q_4}{(W_{\text{net}})_{\text{HE}}}$$

$$Q_4 = (8.375) (W_{\text{net}})_{\text{HE}} = (8.375) (9.93)$$

$$Q_4 = 83.16375 \text{ kW (Maximum amount of heat removal)}$$

(4)

$$Q (W_{net})_{H.E} = (W_{net})_R = (Q_1 - Q_2) = \cancel{Q_3 - Q_4} = Q_3 - Q_4$$

$$\therefore Q_3 = Q_4 + (W_{net})_{H.E} = Q_4 + (W_{net})_{H.E}$$

$$\therefore Q_3 = \text{Heat rejection to ambient} = 83.163 + 9.93$$

$$Q_3 = 93.093 \text{ kW.}$$

Total Heat rejection to ambient, =  $Q_2 + Q_3$

$$\text{Total Heat to ambient} = 3.411 + 93.093 = 96.504 \text{ kW}$$

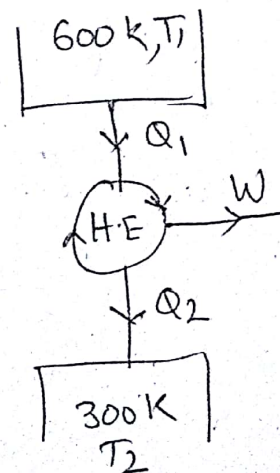
(3) An engine operating on a Carnot cycle works with in temperature limits of 600K and 300K. If the engine receives 2000 kJ of heat, evaluate the work done and thermal efficiency of of Heat engine?

Sol)  $T_1 = 600 \text{ K}, T_2 = 300 \text{ K}$

$$Q_1 = 2000 \text{ kJ}$$

$$\eta_{max} = \eta_{Carnot} = 1 - \frac{T_2}{T_1}$$

$$\eta_{max} = 1 - \frac{300}{600} = 0.5 = 50\%$$



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

$$\Rightarrow W = \text{work output} = \eta Q_1 = (0.5)(2000)$$

$$\text{Work output} = 1000 \text{ kJ}$$

④ \* Two identical bodies of constant heat capacity are at same initial temperature  $T_i$ . A Refrigerator operates between these two bodies until one body is cooled to temperature  $T_2$ . If the bodies remain at constant pressure and undergoes no change of phase, show that minimum amount of work needed to this is

$$W(\text{min}) = C_p \left[ \frac{T_i^2}{T_2} + T_2 - 2T_i \right]$$

sol) The initial temperature of Bodies A, B is  $T_i$ ;  
Final temperature of A, B is  $T_2, T_1$  respectively.

$\therefore$  The heat removed from body A to B with the help of Refrigerator.

(6)

Heat removed from 'A'

$$Q_2 = C_p (T_1 - T_2)$$

Heat rejected to body 'B'

$$Q_1 = W + Q_2$$

$$\Rightarrow W = Q_1 - Q_2$$

$$\therefore \text{but } Q_1 = C_p (T_2 - T_1)$$

$$\therefore W = C_p [(T_2 - T_1) - (T_1 - T_2)]$$

$$W = C_p [T_2 + T_2 - 2T_1] \quad \text{--- (1)}$$

Entropy change of Body 'A' =  $(ds)_A$

$$(ds)_A = \left(\frac{dQ}{T}\right)_A = C_p \int \frac{dT}{T} = C_p \left[ \ln T \right]_{T_1}^{T_2}$$

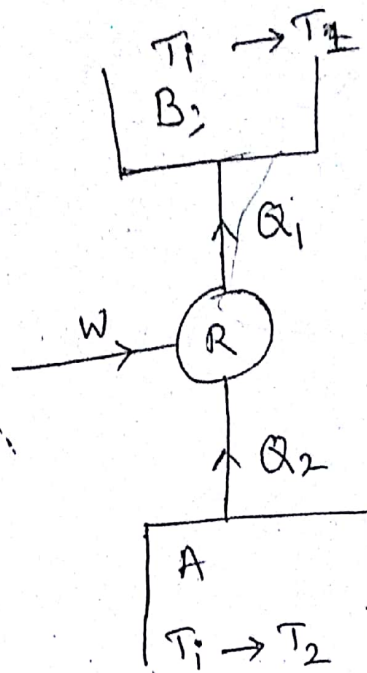
$$(ds)_A = C_p \ln\left(\frac{T_2}{T_1}\right)$$

entropy change of body 'B' =  $(ds)_B$

$$(ds)_B = C_p \ln\left(\frac{T_1}{T_2}\right)$$

Total Entropy  $ds = (ds)_A + (ds)_B$

$$ds = C_p \left[ \ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{T_1}{T_2}\right) \right]$$



(6)

by



entropy principle  $(ds) \geq 0$

$$\therefore C_p \left[ \ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{T_1}{T_1}\right) \right] \geq 0$$

$$C_p \left[ \ln\left(\frac{T_1 T_2}{T_1^2}\right) \right] \geq 0 ; \left[ \begin{array}{l} \therefore \ln(a) + \ln(b) \\ = \ln(a \cdot b) \end{array} \right]$$

for minimum work,  $T_1$  is minimum.

$$\therefore C_p \left[ \ln\left(\frac{T_1 T_2}{T_1^2}\right) \right] = 0 = \ln(1)$$

$$\Rightarrow \therefore \frac{T_1 T_2}{T_1^2} = 1$$

$$\Rightarrow T_1 = \frac{T_1^2}{T_2}$$

Substitute ' $T_1$ ' in (1).

$$W(\min) = C_p \left[ \frac{T_1^2}{2} + T_2 - 2T_1 \right]$$

(5) Two blocks of metal, each having 10 kg and a specific heat of 0.4 KJ/kg-K, are at a temperature of 40°C. A Reversible Refrigerator receives heat from one block

(B)

and rejects to the other. Calculate the work required to cause a temperature difference of  $100^{\circ}\text{C}$ . between the two bodies?

Sol) From the previous derivation.

$$\frac{T_1 T_2}{T_{pr}^2} = 1 \quad \text{--- (a)}$$

$$T_1 = 40^{\circ}\text{C} = 313\text{K}$$

The final temperature of body 1 is  $T_1$ , body 2 is  $T_2$  ( $T_1 > T_2$ )

$$\therefore T_1 - T_2 = 100^{\circ}\text{C} = 100\text{K}$$

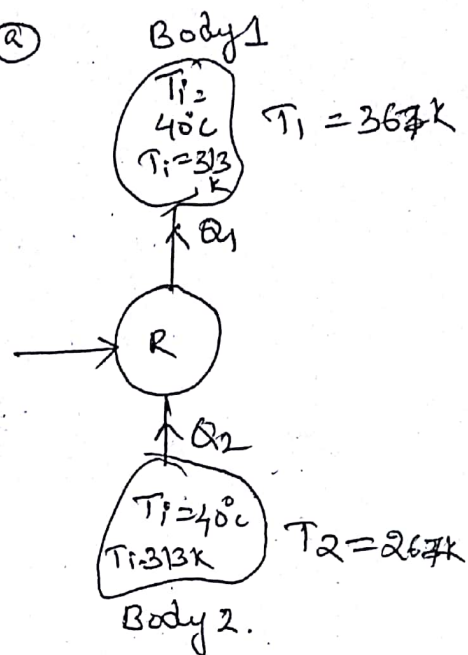
$$\text{(a)} \Rightarrow \frac{T_1 (T_1 - 100)}{T_{pr}^2} = 1$$

$$\Rightarrow T_1 (T_1 - 100) = T_{pr}^2 = (313)^2 = 97969$$

$$\Rightarrow T_1^2 - 100T_1 - 97969 = 0$$

$$\Rightarrow \therefore T_1 = 367, \text{ or } -267$$

$$\therefore T_2 = 267$$



note the work  
difference of  
bodies?

$$Q_2 = m C_p (\Delta T) = m C_p (313 - 267)$$

$$Q_2 = (10)(0.4)(313 - 267) = 184 \text{ KJ}$$

$$\therefore Q_2 = 184 \text{ KJ}$$

$$Q_1 = m C_p \Delta T = (10)(0.4)(67 - 313)$$

$$\therefore Q_1 = 216 \text{ KJ}$$

$$\text{But } Q_1 = Q_2 + W$$

$$\Rightarrow W = Q_1 - Q_2 = (216) - (184) = 32 \text{ KJ}$$

$$\therefore W_{\text{min}} = 32 \text{ KJ}$$

6 Two bodies of equal heat capacities 'C' and temperatures  $T_1$  &  $T_2$  from an adiabatically closed system. what will be the final temperature be if one lets this system come to equilibrium

(i) freely (ii) Reversibly (iii) what is the maximum work which can be obtained from this system?

sol)

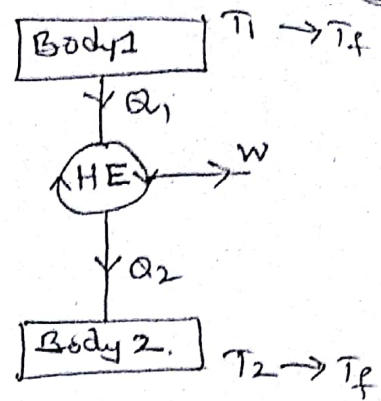
(i) if the two bodies having equal capacities at temperatures  $T_1, T_2$ , the final temperature after obtaining equilibrium

$$T_f = \frac{T_1 + T_2}{2}$$

(ii)

Between two bodies 1, 2,  
→ Introduce a H.E. (Reversible)  
We

→ The final temperature of  
two bodies is  $T_f$



Entropy change for Body 1;  $(ds)_1$

$$(ds)_1 = C_p \ln\left(\frac{T_f}{T_1}\right) \quad \text{--- (a)}$$

Similarly for  $(ds)_2 = C_p \ln\left(\frac{T_f}{T_2}\right)$  --- (b)

$$(ds) = (ds)_1 + (ds)_2$$

$$= C_p \left[ \ln\left(\frac{T_f}{T_1}\right) + \ln\left(\frac{T_f}{T_2}\right) \right]$$

$$(ds) = C_p \ln\left(\frac{T_f^2}{T_1 T_2}\right) \geq 0.$$

$$\therefore ds = 0 \Rightarrow C_p \ln\left(\frac{T_f^2}{T_1 T_2}\right) = 0$$

$$\Rightarrow \ln\left(\frac{T_f^2}{T_1 T_2}\right) = 0 = \ln(1)$$

$$\Rightarrow \frac{T_f^2}{T_1 T_2} = 1 \Rightarrow T_f^2 = T_1 T_2$$

$$\Rightarrow \therefore T_f = \sqrt{T_1 T_2}$$

Q1 = W + Q2 for H.E

Q1 = Cp ΔT = C (T1 - Tf)

Q2 = Cp ΔT = C (Tf - T2)

⇒ W = Q1 - Q2 = C [T1 - Tf - Tf + T2]

W = C [T1 + T2 - 2Tf]

Wmax = C [T1 + T2 - √T1T2]

7) A Copper block of weight 0.4536kg and uniformly heated to 310.7K is dropped in a cold bath where upon it cools to 267K. Calculate the entropy change of the ball for the process (Cp = 0.39 kJ/kg-K)

Sol) Given that m = 0.4536 kg

initial temperature (T1) = 310.7 K

Final temperature (T2) = 267 K

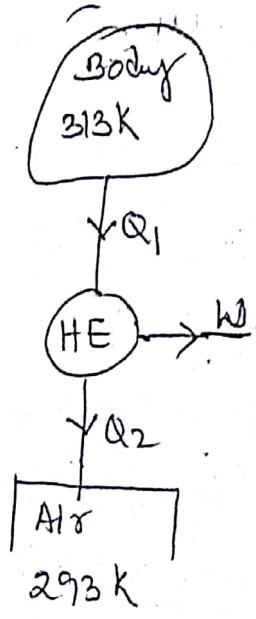
Entropy change (ΔS) = mc\_p ln(T2/T1) = (0.4536)(0.39) [ln(267/310.7)]

ΔS = -0.0268 kJ/K

12  
 (8) Aluminium block ( $C_p = 0.4 \text{ kJ/kg-K}$ ) with a mass of  $5 \text{ kg}$  is initially at  $70^\circ\text{C}$  in a room Air at  $20^\circ\text{C}$ . It is cooled reversibly by transferring heat to a completely cyclic heat engine until block reaches  $20^\circ\text{C}$ . The  $20^\circ\text{C}$  room air serves as a constant temperature sink for the engine. compute (i) change in entropy of block, (ii) the change in entropy of air (iii) work done by engine?

Sol

(i) Body Temperature ( $T_1$ ) =  $313 \text{ K}$   
 Air temperature ( $T_2$ ) =  $293 \text{ K}$ .  
 final temperature of body  $T_2'$ .



$$(ds)_{\text{body}} = m c_p \ln\left(\frac{T_2}{T_1}\right)$$

$$= (5)(0.4) \ln\left(\frac{293}{313}\right)$$

$$(ds)_{\text{body}} = -0.132 \text{ kJ/K}$$

the entropy change of air:  $(ds)_{\text{air}}$

$$(ds)_{\text{air}} = \frac{Q_2}{T_2} = \frac{Q_1 - W}{T_2}$$

$$Q_1 = (5)(0.4)(313 - 293) = 40 \text{ KJ}$$

$$(ds) = (ds)_{\text{body}} + (ds)_{\text{air}} \geq 0$$

$$\Rightarrow m c_p \ln\left(\frac{T_2}{T_1}\right) + \frac{Q_1 - W}{T_2} \geq 0$$

$$\Rightarrow m c_p \ln\left(\frac{T_2}{T_1}\right) + \frac{m c_p (T_1 - T_2) - W}{T_2} = 0$$

$$\begin{aligned} \Rightarrow W &= m c_p \left[ T_2 \ln\left(\frac{T_2}{T_1}\right) + (T_1 - T_2) \right] \\ &= (5)(0.4) \left[ (293) \ln\left(\frac{293}{313}\right) + (313 - 293) \right] \end{aligned}$$

$$W = 1.306 \text{ KJ}$$

$$\therefore (ds)_{\text{air}} = \frac{Q_1 - W}{T_2} = \frac{40 - 1.306}{293} = 0.132 \text{ KJ/K}$$

(iii) work developed  $(W) = 1.306 \text{ KJ}$