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Chandra Prakash Suanr

Chapter-9

Laws of Thermodynamics and Their APP.

Zeroth law

"If two systems are in thermal equilibrium with a third system then they must be in thermal equilibrium with each other." This statement is known as zeroth law of thermodynamics and forms the basis of concept of temperature as shown in figure.

Fig : diagram for zeroth law

First law of Thermodynamics

First statement :

It states that, if in th process of converting heat energy into mechanical energy certain amount of heat disappears then equivalent amount of work is done.

Thus, if w is the amount of work, then amount of heat q, that can be produced by

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it is given by $W = JQ$

Second statement:

If ΔQ is heat supplied to a body then that heat is spent in three ways:-

a. to increase internal K.E.

b. to increase internal P.E of the system

c. to do the external work.

If ΔU_K and ΔU_P be internal K.E and P.E of the system respectively. And ΔW be the external workdone then,

$$\Delta Q = \Delta U_K + \Delta U_P + \Delta W$$

$$\therefore \Delta Q = \Delta U + \Delta W \quad [\because \Delta U = \Delta U_K + \Delta U_P]$$

Hence, the total heat energy supplied in a system should be equal to the sum of change in internal energy of the system and amount of workdone in the system.

Second law of Thermodynamics

Kelvin statement:

It states that it is impossible to get a continuous supply of heat from a body by cooling it to a temperature lower than that of coldest of its surrounding. For eg: heat engine.

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Clausius statement:

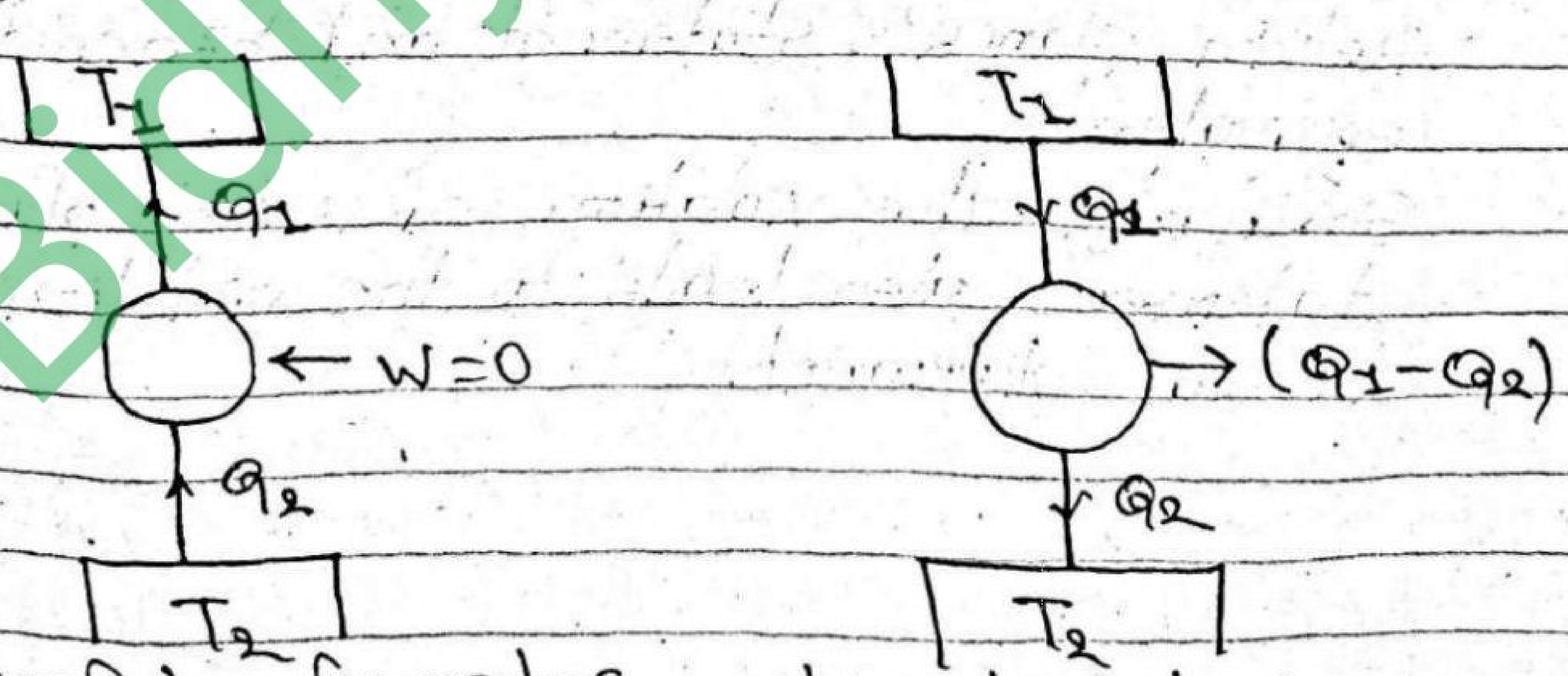
It states that it is ~~impo~~ impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance.
For eg: ammonia ice plant.

Comparison between 1st and 2nd law

The first law of thermodynamics does not give the direction of flow of heat. It only gives the relation between the workdone and heat produced.

But the second law of thermodynamics gives the conditions under which heat can be converted into work.

Two statements of second law are equivalent



(a) perfect refrigerator (b) practical heat engine

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Consider a perfect refrigerator in against is clausius statement of second law of thermodynamics. That means it absorbs Q_2 heat from sink and transferred to source without any external work.

Again, we consider a heat engine according to kelvin planck statement. Then it absorbs Q_1 heat from source, performs $(Q_1 - Q_2)$ external work and rejects Q_2 heat to sink.

Now, the two devices are coupled, then for the couple device $= Q_1 - Q_2$

Net heat absorbs from source $= Q_1 - Q_2$

Net heat rejected to sink $= 0$

That means the couple device works like a perfect heat engine which violets the kelvin planck's statement. Therefore, violation of clausius statement gives to violation of kelvin planck's statement and hence they are equivalent.

Similarly, the violation of kelvin planck's statement also leads to the violation of clausius statement.

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Carnot's reversible engine

It consists of

1. Source: The source should be at a fixed high temperature T_1 from which the heat engine can draw heat.
2. Sink: It should be fixed to a low temperature T_2 to which any amount of heat can be rejected.
3. Working substance: A cylinder with non-conducting sides and conducting bottom contains the perfect gas as the working substance. It consists of non-conducting frictionless piston. It is provided with a non-conducting stand.

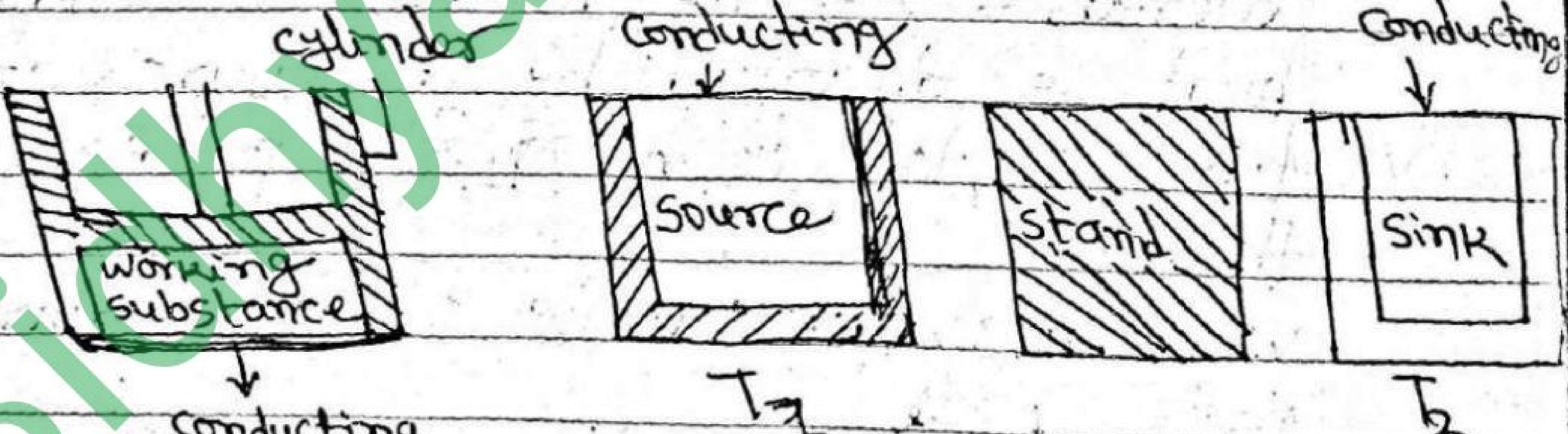

Fig: Carnot engine

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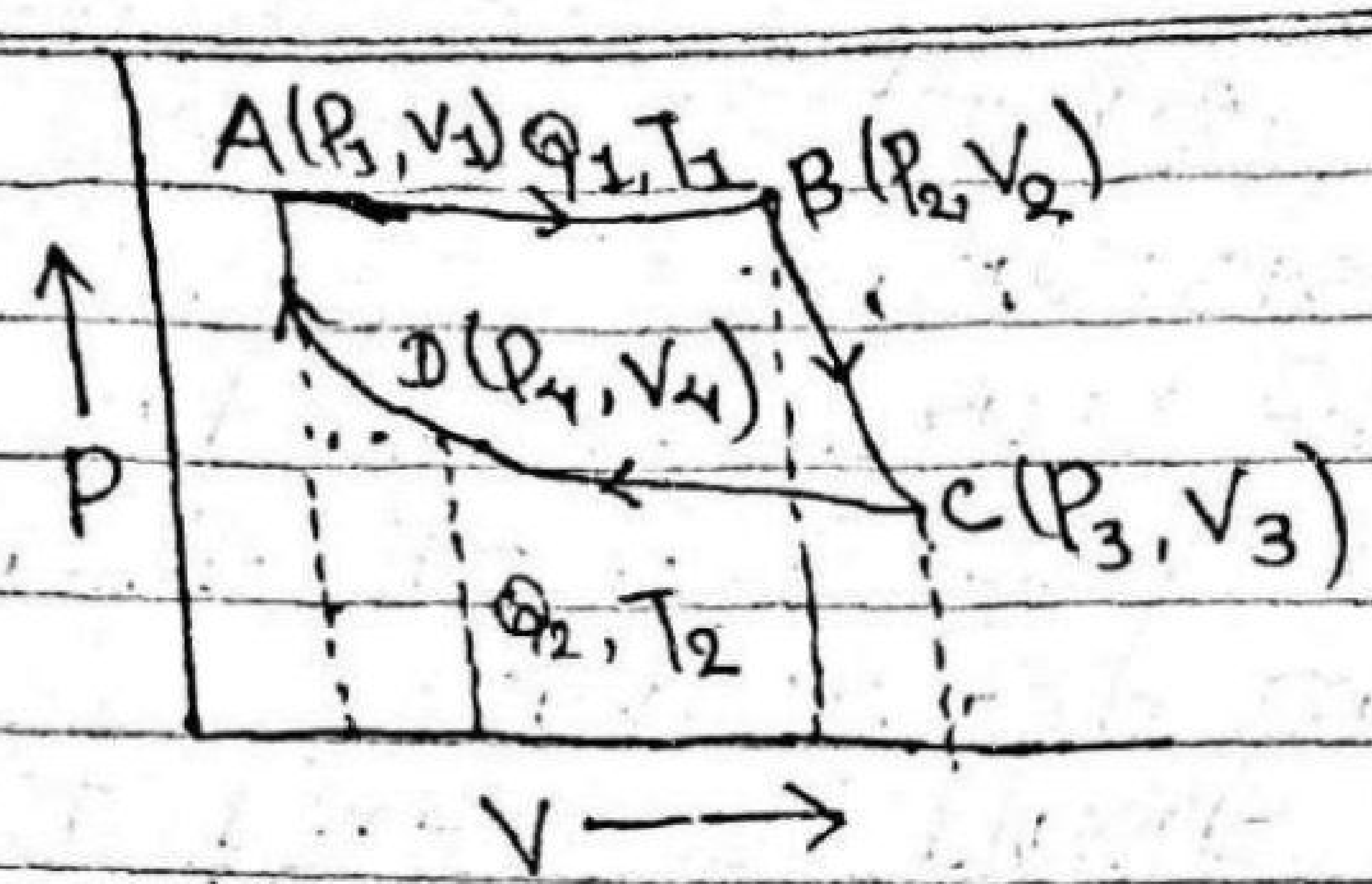

Fig: PV diagram for carnot engine

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Carnot's cycle

1. Place the engine containing working substance over the source at temperature T_1. Its pressure is P_1 and volume is ~~P_1~~ V_1 at A as shown in figure. Decrease the pressure so that the volume of substance increases. As the bottom is conducting heat is absorbed by the source at temperature T_1, let it be Q_1. The process is isothermal.

   Workdone for 1 mole of gas from A to B is

$$W_1 = \int_{V_1}^{V_2} P dv = R T_1 \ln \frac{V_2}{V_1} \longrightarrow (1)$$

2. Place the engine on the insulating stand. Decrease the pressure is P_3 and volume is V_3. The process is adiabatic process.

Workdone is done by the gas. The temperature falls from T_1 to T_2 and workdone from B to C is

$$W_2 = \int_{V_2}^{V_3} PdV = \frac{P_3V_3 - P_2V_2}{1-\gamma} = \frac{RT_2 - RT_1}{1-\gamma}$$

$$\therefore W_2 = \frac{R(T_1 - T_2)}{\gamma - 1}$$

3. place the engine on sink at temperature T_2. Increase the pressure. work is done on working substance. Here the process is isothermal due to conducting base of sink. A quality of heat rejected to sink is Q_2.
Workdone from C to D

$$W_3 = \int_{V_3}^{V_4} PdV = RT_2 \ln \frac{V_4}{V_3}$$

$$W_3 = -RT_2 \ln \frac{V_3}{V_4} \longrightarrow (3)$$

4. Place the engine in an insulating stand. Increase the pressure, so volume decreases. Hence, the process is completely adiabatic. The temperature rises and finally the point A is reached hence a complete cycle ABCDA is obtained. Workdone from D to A is

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$$W_4 = \int_{V_4}^{V_1} p\,dV = -\frac{R(T_1-T_2)}{\gamma-1} \longrightarrow (4)$$

Net amount of workdone in one complete cycle ABCDA is given as

$$W = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \ln\frac{V_2}{V_1} + \frac{R(T_1-T_2)}{\gamma-1} - RT_2 \ln\frac{V_3}{V_4} - \frac{R(T_1-T_2)}{\gamma-1}$$

$$W = RT_1 \ln\frac{V_2}{V_1} - RT_2 \ln\frac{V_3}{V_4} \longrightarrow (5)$$

As point A and D are at same adiabatic

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

i.e $\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \longrightarrow (6)$

~~From eq^n (6) and (7)~~

$$\frac{V_4}{V_1} = \frac{V_2}{V_3}$$

The point B and C are on same adiabatic.

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

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$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \longrightarrow (7)$$

from eqⁿ (6) and (7)

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

or, $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

Now, from eqⁿ (5).

$$W = RT_1 \ln\frac{V_2}{V_1} - RT_2 \ln\frac{V_2}{V_1}$$

$$= R(T_1 - T_2)\ln\frac{V_2}{V_1}$$

$\therefore W = Q_1 - Q_2$ = Net amount of heat absorbed by the working substance.

$\therefore$ Efficiency, $\eta = \frac{\text{useful output}}{\text{Input}}$

$$= \frac{W}{Q_1}$$

$$= \frac{Q_1 - Q}{Q_1}$$

$$= \frac{R(T_1 - T_2)\ln\frac{V_2}{V_1}}{RT_1 \ln\frac{V_2}{V_1}}$$

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

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

The carnot engine is perfectly reversible. It can be oprated in reverse direction also, then it works as a refrigerator. All practical engines have efficiency less than the carnot's engine.

Carnot's theorem

It consiststs of

1. No engine can be more efficient than a perfectly reversible engine (carnot's engine) working between the two same temperatures.
2. The efficiency of all reversible engines working between the same two temperature is same whatever the working substance.

Proof (1)

Consider two engine one is reversible R and another is irreversible I working between the temperatures T_1 and T_2 ($T_2 > T_2$) as shown in figure(i). The irreversible engine absorbs Q_1 amount of heat from source

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at temperature T_1 and performs the output work W and reject $(Q_1 - W)$ amount of heat to sink at temperature T_2.

Similarly engine R absorbs Q_1' amount of heat from source at temperature T_1 performs output work W and then rejects $(Q_1' - W)$ amount of heat to sink. Then the efficiency of irreversible engine is

$$\eta_{irr} = \frac{W}{Q_1} \longrightarrow (1)$$

And the efficiency of reversible engine is

$$\eta_{rev} = \frac{W}{Q_1'} \longrightarrow (2)$$

Let assume irreversible is more efficient than the reversible engine. Then,

$$\eta_{irr} > \eta_{rev}$$

or, $\dfrac{W}{Q_1} > \dfrac{W}{Q_1'}$

or, $Q_1' > Q_1 \longrightarrow (3)$

Now, we ~~we~~ couple these two engine by a belt in such a way that Engine I is working heat engine and engine R is working as a refrigerator as shown in figure. The source now loses Q_1 heat to I and gains Q_1' from R.

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$\therefore$ Heat gained by the source $= Q_1' - Q_1$ — (4)

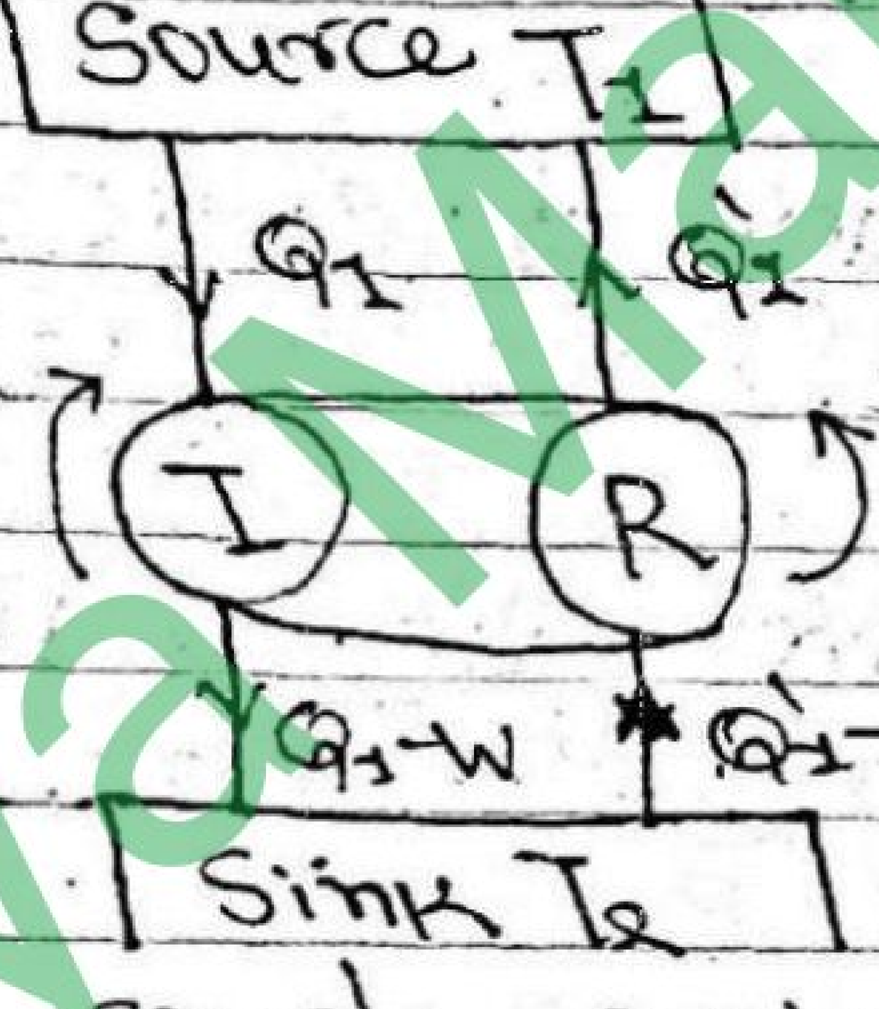
The sink gains $(Q_1 - W)$ heat ~~from~~ I and loses $(Q_1' - W)$ to R.

$\therefore$ Heat lost by sink $= (Q_1' - W) - (Q_1 - W)$

$= (Q_1' - Q_1)$

$= +ve$ (from 3)

External work done on the system $= 0$



Thus the couple engine perform a self acting machine unaided by external agency transfer heat continuously from a body at low temperature to higher temperature. This conclusion contradicts the 2^{nd} law of thermodynamics and hence our assumptions is incorrect. So, we ~~can~~ conclude that no engine can be more efficient than a perfectly reversible engine working betn the same two temperature.

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Proof(2):

To prove the 2^{nd} part of the theorem we replace the irreversible engine by another reversible engine R' proceeding as in the 1^{st} part of the theorem and ~~on assumption~~ assuming the engine R' is more efficient than the engine R, we will reach the stage that will contradicts the second law of thermodynamics. Therefore our assumptions $\eta_{R'} > \eta_R$ must be wrong.

Again considering the engine R is more efficient than the engine R', we would obtain the same situation that will also violate the 2^{nd} law of thermodynamics. That means our assumptions $\eta_R > \eta_{R'}$ must be wrong.

Hence we can conclude that η_R must be equal to the $\eta_{R'}$ i.e. $\eta_R = \eta_{R'}$.

Which shows that all reversible engine working between same temperature limits are equally efficient.

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Absolute scale of temperature.

The efficiency of a reversible carnot's engine depends upon the two temperature between which it works and is independent of the properties of the working substance. Thus there is a property which absolutely depends on temperature only. so a temp. scale based on the working of a carnot's engine is a standard scale called absolute scale of temperature. Lord Kelvin worked out of such an absolute scale known as Kelvin's thermodynamical scale.

Suppose an engine works between the temperature θ_1 and θ_2. Let Q_1 is the heat absorbed at θ_1 and Q_2 is the heat rejected at θ_2.

$$\eta = f(\theta_1, \theta_2)$$

$$\eta = \frac{Q_1 - Q_2}{Q_1} = f(\theta_1, \theta_2)$$

i.e. $1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$

or, $\frac{Q_2}{Q_1} = 1 - f(\theta_1, \theta_2)$

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$$\therefore \frac{Q_1}{Q_2} = \frac{1}{1 - f(\theta_1, \theta_2)} = F(\theta_1, \theta_2) \longrightarrow (1)$$

Where F is some other function of temp.

Similarly, if the engine works between the temperature θ_2 and θ_3 and Q_2 and Q_3 be the heat absorbed and rejected at that temperatures then,

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3) \longrightarrow (2)$$

Again, for the temp. θ_1 and θ_3, the heat absorbed is Q_1 and rejected is Q_3

$$\therefore \frac{Q_1}{Q_3} = F(\theta_1, \theta_3) \longrightarrow (3)$$

From eq^n (1), (2) and (3), we get

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3}$$

or, $F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3)$

Here L.H.S is only the function of θ_1 and θ_2 whereas right hand side is function of $\theta_1, \theta_2, \theta_3$. So, let us choose F such that

$$\therefore F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

$$F(\theta_2, \theta_3) = \frac{\phi(\theta_2)}{\phi(\theta_3)}$$

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$$F(\theta_1,\theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_3)}$$

Where ϕ is another function of temp.

$$\therefore \frac{Q_1}{Q_2} = F(\theta_1,\theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \rightarrow (4)$$

The expression on R.H.S. represents the ratio of two kelvin temperatures and this can be denoted by $\frac{T_1}{T_2}$.

$$\text{So, } \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \longrightarrow (5)$$

The relation (5) is used to represent a new scale and this does not depend upon the property of the working substance

$$\therefore \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

Since $(Q_1 - Q_2)$ gives the output work per cycle by the reversible engine operating between the two temperature T_1 and T_2, the temperature are measured in terms of work and hence this scale is also known as work scale of temperature.

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Entropy changes in reversible process and irreversible process

⇒ Solution,

Entropy is a thermodynamics variable just like other thermodynamics variables pressure, volume, temperature, and internal internal energy, which measure the disorderness or randomness of the system.

On comparing, the solid, liquid and gas, the solid is more ordered than liquid and liquid is more ordered than gas. So, the entropy of solid is less than liquid and gas and entropy of liquid is less than that of gas.

Let dq be the amount of heat added to the system at temperature T then the ratio $\frac{dq}{T}$ is defined as the entropy of the system denoted by ds i.e. $ds = \frac{dq}{T}$

For adiabatic process, dq = 0 then
ds = 0

∴ S = Constant i.e. entropy is ~~entropy~~ constant.

When heat is absorbed during a process, there is increase in entropy and vice-versa.

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Change in entropy in reversible process (carnot cycle)

Consider a complete reversible process ABCDA. From A to B heat is absorbed by working substance at the temperature T_1. The gain in entropy of the working substance from A to B $= \frac{Q_1}{T_1}$

Fig: ~~fig~~ PV-diagram for reversible process

From B to C and D to A there is no change in entropy because B to C and D to A is adiabatic. The loss ~~of~~ of working substance from C to D

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

Thus total gain in entropy by the working substance on the cycle ABCDA

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

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But, for a complete reversible process

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

$$\therefore \frac{Q}{T} = \text{Constant}$$

Hence, total increase in entropy of working substance in a complete reversible process

$$ds = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

Hence, entropy remains constant during reversible process.

Change in entropy in an irreversible process

In an irreversible process by the conduction ~~of~~ or radiation, heat is lost by a body at a higher temperature T_1 and is gained by the body at a lower temperature T_2. Here $T_1 > T_2$. Let the quantity of heat given out by body at temperature T_1 be ~~Q_1~~ Q and the heat gained by the body at temperature T_2 be Q. Consider the hot and cold bodies as a single system.

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Loss in entropy of hot body $= \frac{Q}{T_1}$

Gain in entropy of cold body $= \frac{Q}{T_2}$

Total increase in entropy of system

$= \frac{Q}{T_2} - \frac{Q}{T_1}$

Since $\frac{Q}{T_2} > \frac{Q}{T_1}$, it is a positive quantity and thus entropy of system increases in all irreversible process.

Entropy and the second law

According to the kelvin planck ~~sta~~ statement of 2nd law of thermodynamics. "There is no any engine which can convert total quantity of heat (Q) taken from the source at a single temp. T into work." If it be so then there would be decrease in entropy of the source by an amount $\frac{Q}{T}$, where as the entropy of the working substance remains constant because it returns to the intial state after completeing the cycle. Thus the

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entropy of the system plus surrounding would decrease which is against the principles of increase of entropy.

In the same way according to clausius statement "there will be no any refrigerator which can transfer heat from a colder body at temperature T_2 to a higher (hotter) body at temperature T_1 without ~~can~~ an external agency. If it is so, the entropy of colder body will decrease and the entropy of hotter body will increase.

Decrease in entropy $= Q/T_2$

Increase in entropy $= Q/T_1$

Here $T_1 > T_2$

So, $\frac{Q}{T_2} > \frac{Q}{T_1}$

The total entropy of the system plus surrounding would decrease by $\left(\frac{Q}{T_2} - \frac{Q}{T_1}\right)$

which is against the entropy principle.

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Third law of thermodynamics

The disorder of the molecules increases due to the increase in entropy. As temperature falls, the entropy decreases and thus disorderness of the molecules decreases.

At absolute zero of temperature, the disorderness completely disappears and the molecules are in perfect order i.e. the entropy is zero. This is known as 3rd law of thermodynamics.

Physical significance of entropy

It is difficult to form a physical concept of entropy as there is nothing physical to represent it and it cannot be felt like temperature or pressure. But, we have

$$\text{change in entropy} = \frac{\text{Heat added or substracted}}{\text{Absolute temperature}}$$

We may say that heat energy has the same dimension as the product of entropy and absolute temperature since the gravitational potential energy of a body is proportional to the product of its mass

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and height above some zero level hence if we may take temperature equivalent to height we may ~~take~~ regard entropy as analogous to mass or inertial. In this way, we may think of entropy as thermal inertia which bears to heat motion a relation similar to that which ~~bear~~ mass bear to linear motion or moment of inertia bears to rotational motion.

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Chandra Prakash Suanr
Bidhya Mandir
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