

Chapter 3

Second law of thermodynamics and Entropy

~~Second law of thermodynamics is consequent to evidence~~

~~Statement:~~

~~Heat can never spontaneously transfer from colder object to a warmer object.~~

The second law of thermodynamics states the limits and conditions for the conversion of heat energy into the other energy.

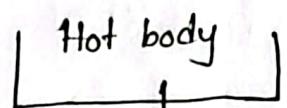
~~Kelvin - Planck statement:~~

"It is impossible to construct a device which operates on a cycle and produces no other effect than the transfer of heat

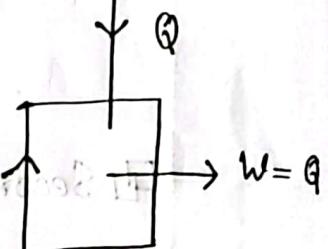
from a single body and production of equivalent amount of work."

The second law implies that some heat must also be rejected by the device to a body at a lower temperature as in the heat engine.

otherwise, one could have an engine with 100% efficiency.



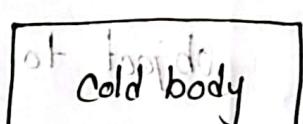
If the Kelvin statement were untrue, a number of impossible consequences would result. For example, a ship could be driven across the sea just by extracting heat from the sea and converting it entirely into work.



Electric lights could be lit using thermal energy from the surrounding air.

Not allowed

But this couldn't be done, because the Kelvin statement seems to be valid in general.



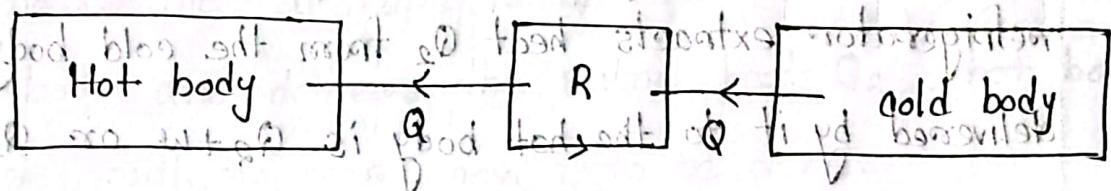
~~It is impossible to construct a device that operating in a cycle, produce no effect other than, the transfer of heat from a colder body to a hotter body.~~

~~Clasius statement:~~

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

This form of the second law tells us, work must be

④ performed if heat is to be transferred from a colder to a hotter body. When this is not so, house could be heated just by cooling the outside air at no cost, with slaves + no work having it to be done gratis with the help of salt aqueous solns. also no expenditure of work or heat will be lost.



Heat cannot spontaneously flow from cold system without external work being performed on the system.

Equivalence of Kelvin and Clausius statement :

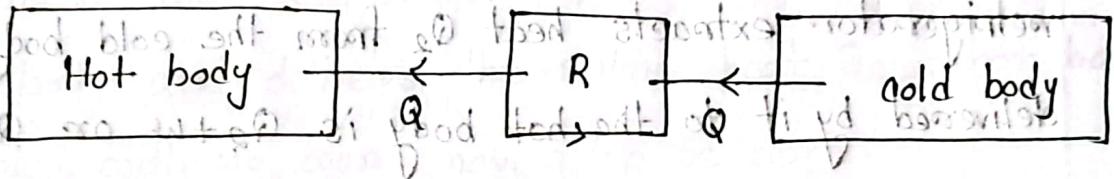
The equivalence of two statements will be proved if it can be shown that violation of one statement implies the violation of second and vice-versa.

Let us consider a heat engine converting all the heat it receives from high temperature reservoir into work.

Thus violating Kelvin-Plank statement here is equivalent

to violating Clausius statement.

is performed if heat is to be transferred from a colder to a hotter body. When this is not so, house could be heated just by cooling the outside air at no cost, with ~~losses~~ & ~~no work~~ having it to be done ~~without~~ with no extra effort.



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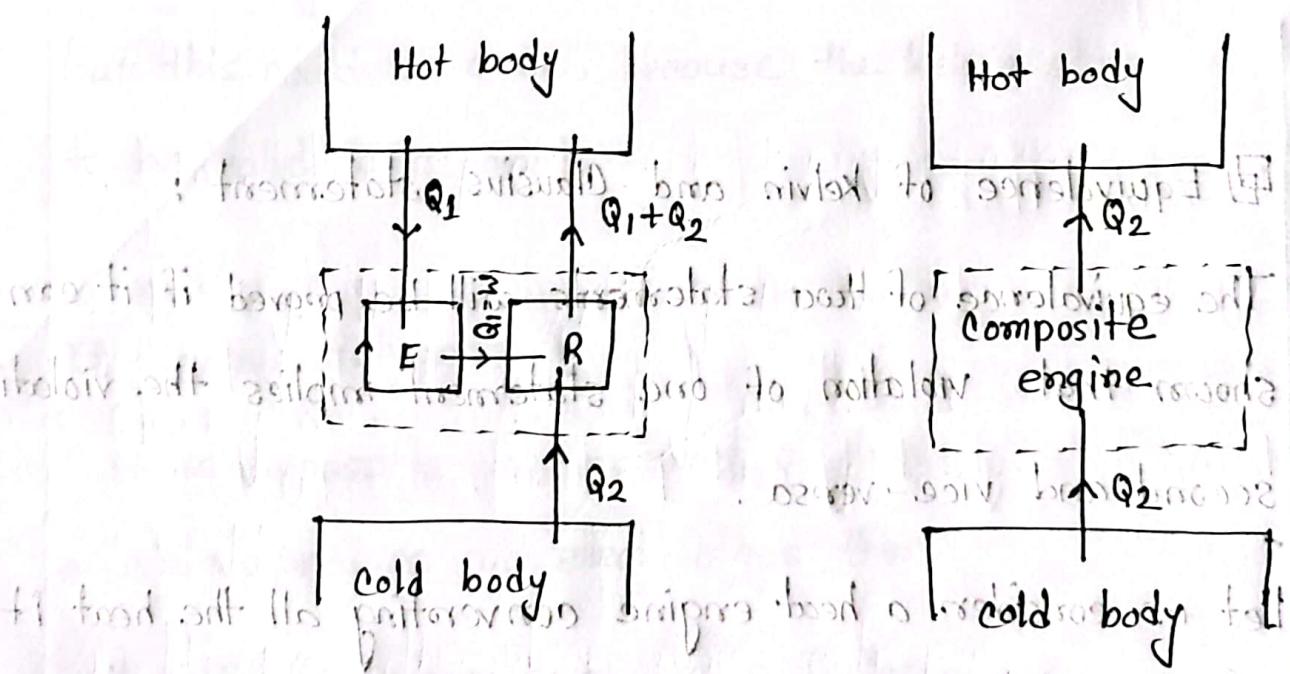
The equivalence of two statements will be proved if it can be shown that violation of one statement implies the violation of second and vice-versa.

Let us consider a heat engine converting all the heat it receives from high temperature reservoir into work.

Thus violating Kelvin-Planck statement, there is no work

which is always not true.

This means that one can have an engine that takes Q_1 heat from a hot body and delivers work $w = Q_1$ in one cycle. Let this engine drive a refrigerator R . Now adjust the size of the working cycles so that it is sufficient work to drive the refrigerator through one cycle. Suppose the refrigerator extracts heat Q_2 from the cold body. Then the heat delivered by it to the hot body is $Q_2 + w$ or $Q_1 + Q_2$. It is useful to regard the engine and the refrigerator as the composite engine.

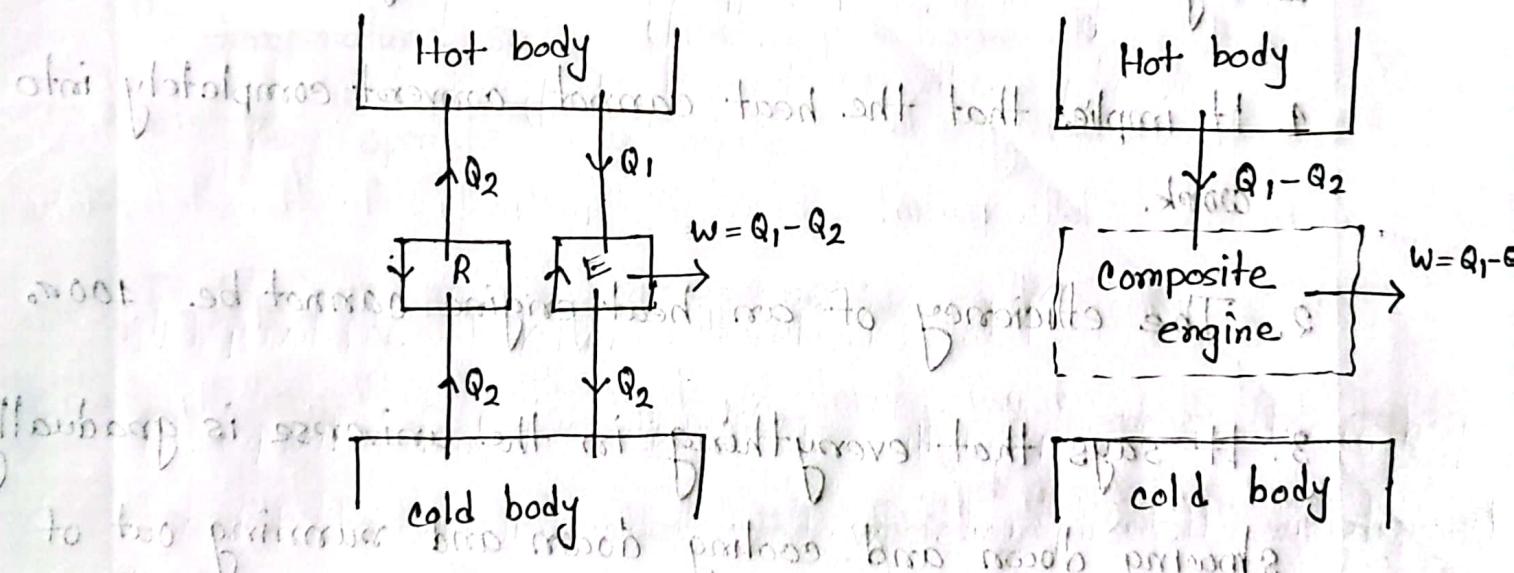


This composite engine extracts Q_2 from the cold body and delivers a net amount of heat, $Q_2 + Q_1 - Q_1 = Q_2$, to the hot body, but no work is done.

describing. Hence there is a violation of the clausius statement.

Now let us consider an heat engine which is transferring heat from cold body to a hot body without any extennal work. Thus violating the clausius statement.

This means that a refrigerator that extracts heat Q_2 from a cold body and delivers the same heat Q_2 a hot body in one cycle, with no work having to be done.



Now let an engine operate between the same two bodies,

Adjust the size of its working cycle so that in one cycle it extracts heat Q_1 from the hot body, give up the same heat Q_2 to the cold body as was extracted by the refrigerator and so delivers the work $w = Q_1 - Q_2$. The engine and the

refrigerator may be regarded as the composite engine, which takes in heat $Q_1 - Q_2$ from the hot body and delivers the same amount of work. Hence there is a violation of the Kelvin statement.

This proves the equivalence of the two statements.

■ Significance of second law of thermodynamics:

1. It implies that the heat cannot convert completely into work.

2. The efficiency of an heat engine cannot be 100%.

3. It says that everything in the universe is gradually slowing down and cooling down and running out of energy.

4. It gives the idea about entropy.

Entropy is a measure of disorder or randomness in a system. It is represented by the symbol S.

E Heat engine :

Any mechanism for the conversion of heat into mechanical power is called heat engine.

They are characterised by followings -

1. They receive heat from a high temperature source.
2. They convert part of this heat into work.
3. They reject the remaining waste heat to a low temperature sink.

4. They operate in a cycle.

E Efficiency of a heat engine :

The ratio of the work done, w by a heat engine to the receive heat Q is called the efficiency of the heat engine.

$$\eta = \frac{w}{Q} \times 100\%$$

$w = \text{work done}$

$Q = \text{Given heat}$

(state 1) & state 2 of (T_1, V_1, P_1) & state 3 of (T_2, V_2, P_2)

Q1) Carnot cycle : ..

A carnot cycle is defined as an ideal reversible closed thermodynamic cycle in which there are four successive operations involved, which are isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression.

During these operations, the expansion and compression of substance can be done up to the desired point and back to the initial state.

Step 1 : Isothermal expansion :

Let the working substance during isothermal expansion goes from its state initial state $A(P_1, V_1, T_1)$ to the state $B(P_2, V_2, T_1)$ at constant temperature T_1 along AB . In this process, the substance absorbs heat Q_1 from the source at T_1 and does work W_1 given by,

$$Q_1 = W_1 = \int_{V_1}^{V_2} P dV = RT_1 \log_e \frac{V_2}{V_1} = \text{area } ABCEA$$

Step 2 : Adiabatic expansion :

This operation is represented by the adiabatic BC , starting from the initial state $B(P_2, V_2, T_1)$ to the state $C(P_3, V_3, T_2)$.

In this process, there is no transfer of heat, the temperature of the substance falls to T_2 and it does some external work

W_2 given by,

$$W_2 = \int_{V_2}^{V_3} P dV = K \int_{V_2}^{V_3} \frac{dV}{V^\gamma}$$

[During adiabatic process $PV^\gamma = \text{constant} = K$]

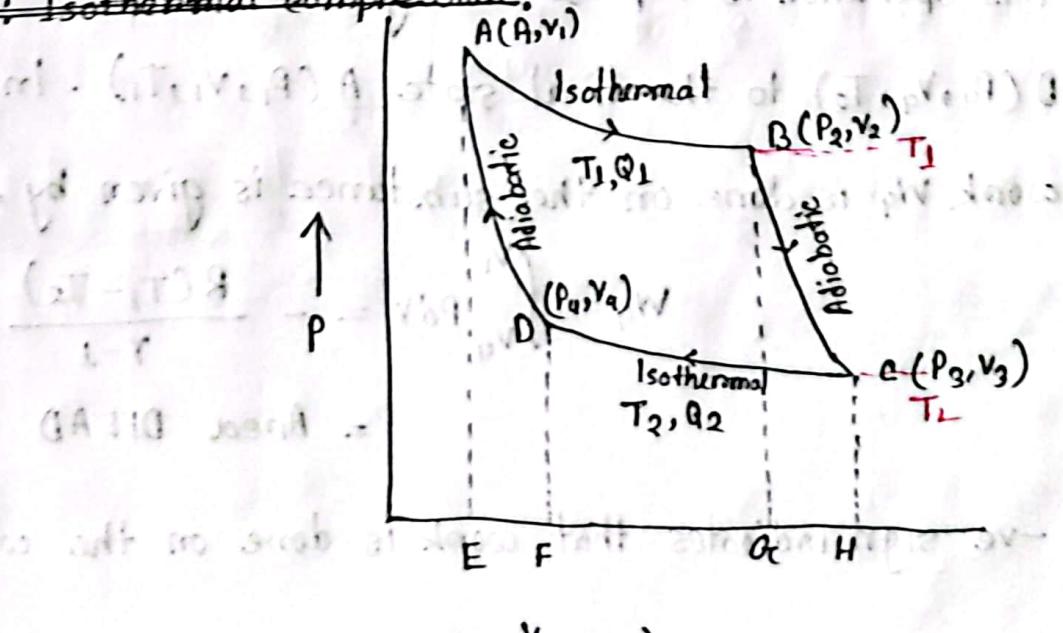
$$= \frac{K V_3^{1-\gamma} - K V_2^{1-\gamma}}{1-\gamma}$$

$$= \frac{P_3 V_3 - P_2 V_2}{1-\gamma} = \quad [\because P_2 V_2^\gamma = P_3 V_3^\gamma = K]$$

$$= \frac{RT_2 - RT_1}{1-\gamma}$$

$$= \frac{R(T_2 - T_1)}{1-\gamma} = \text{Area } BEHG$$

~~Step 3: Isothermal compression:~~



Step 3: Isothermal compression:

This operation is represented by the isothermal CO₂, starting from the state C (P₃, V₃, T₂) to the state D (P₄, V₄, T₂). In this process, the substance rejects heat Q₂ to the sink at T₂ and work W₃ is done on the substance given by,

$$Q_2 = W_3 = \int_{V_3}^{V_4} P dV = RT_2 \log_e \frac{V_4}{V_3}$$

$$= -RT_2 \log_e \frac{V_3}{V_4} = \text{area CHFDC}$$

[+ve sign indicates that work is done on the working substance.]

Step 4: Adiabatic compression:

This operation is represented by adiabatic DA, starting from D (P₄, V₄, T₂) to the final state A (P₁, V₁, T₁). In this process, work W₄ is done on the substance is given by,

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

= Area of DFEAD

-ve sign indicates that work is done on the working substance

$\leftarrow V$

Therefore net work done,

$$\text{Work between A and D} = W = W_1 + W_2 + W_3 + W_4$$

$$\therefore \text{Work done} = W_1 + W_3 = \boxed{Q_1 - Q_2} = \text{Area } ABCD$$
$$= \cancel{Q_1} - \cancel{Q_2} = \text{Area } ABCD$$

$$= RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_3}{V_4}$$

Since A and D lie on the same adiabatic DA

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

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_4} \right)^{\gamma-1}$$

Similarly, point B and C lie on same adiabatic BC

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

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

$$\Rightarrow \left(\frac{V_1}{V_4} \right)^{\gamma-1} = \left(\frac{V_2}{V_3} \right)^{\gamma-1}$$

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

$$\therefore \text{Net work, } W = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_2}{V_1}$$

$$= R(T_1 - T_2) \log_e \frac{V_2}{V_1} = Q_1 - Q_2$$

④ Carnot efficiency :

The efficiency is the ratio of quantity of heat converted into work per cycle of the total amount of heat absorbed.

$$\eta = \frac{\text{Work}}{\text{Input}} = \frac{W}{Q_1}$$

$$\Rightarrow \eta = \frac{Q_{21} - Q_2}{Q_1}$$

$$\Rightarrow \eta = \left(1 - \frac{Q_2}{Q_1}\right) \quad (1)$$

We know that,

$$\Rightarrow \frac{Q}{T} = \text{constant}$$

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

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

$$\text{From (1), } \eta = 1 - \frac{T_2}{T_1} \quad (2)$$

From this we can see that efficiency of Carnot engine depends only upon the temperature of source and the sink.

Ques. Why the efficiency of an Carnot heat engine (ideal heat engine) can not be 100%.

⇒ The efficiency of a Carnot engine is,

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

where, Q_1 and Q_2 respectively are heat extracted from the source and heat rejected to the sink.

The efficiency can be 1 or 100%, only when $Q_2 = 0$; i.e; no

heat is rejected to the sink. This fact is denied by second

law of thermodynamics according to which, it is impossible

to construct a heat engine, operating in cycles, which converts the whole of the heat energy extracted from the source.

That means Q_2 can't be zero. and so the efficiency cannot be 100%.

Again from the equation it is clear that $Q_1 > Q_1 - Q_2$

which means efficiency can't be 100%.

so the final answer is that efficiency can't be 100%.

Ans. Therefore, efficiency

→ Why is the efficiency of a carnot engine η_{Carnot} maximum?

⇒ We know, the efficiency of a carnot engine,

$$\eta = 1 - \frac{T_H}{T_C} = 1 - \frac{Q_2}{Q_1}$$

where T_H and T_C are fixed temperature at the hot and cold

reservoirs respectively.

$$Q_1 - Q_2 < 0$$

Let us consider the 3 cases:

1. If the heat engine is more efficient than a carnot engine, $\eta_E > \eta_{\text{Carnot}}$

then the heat extracted of the two reservoirs $Q_{\text{net}} < 0$.

This corresponds to the sole effect as the carnot fridge plus

heat engine being a ~~heat~~ transfer of heat from the cold

reservoir to the hot one. This would violate the second law

and thus this level of efficiency is impossible.

2. If the efficiency of an arbitrary engine η_E is such that

$\eta_E = \eta_{\text{Carnot}}$ then the net heat transfer is zero and

everything is transferred back to its initial state after

one cycle implying with this efficiency the process is

completely reversible.

3. If $\eta_E < \eta_C$ then $Q_{net} > 0$, so the cycle involves at most transfer of heat from the hot reservoir to the cold one.

This is of course fine but to restore the reservoirs to their original state would require a shifting of the heat back thus this process is irreversible.

So from these three case we conclude that no heat engine operating between two reservoirs can have a great efficiency than a ~~Carnot~~ engine.

$$\frac{W}{Q_1} < \frac{W}{Q_2}$$

$$W < Q_2 \text{ or } W < Q_1$$

~~Cannot~~ Carnot theorem:

Statement: No engine operating between two reservoirs can be more efficient than a Carnot engine operating between those same two reservoirs.

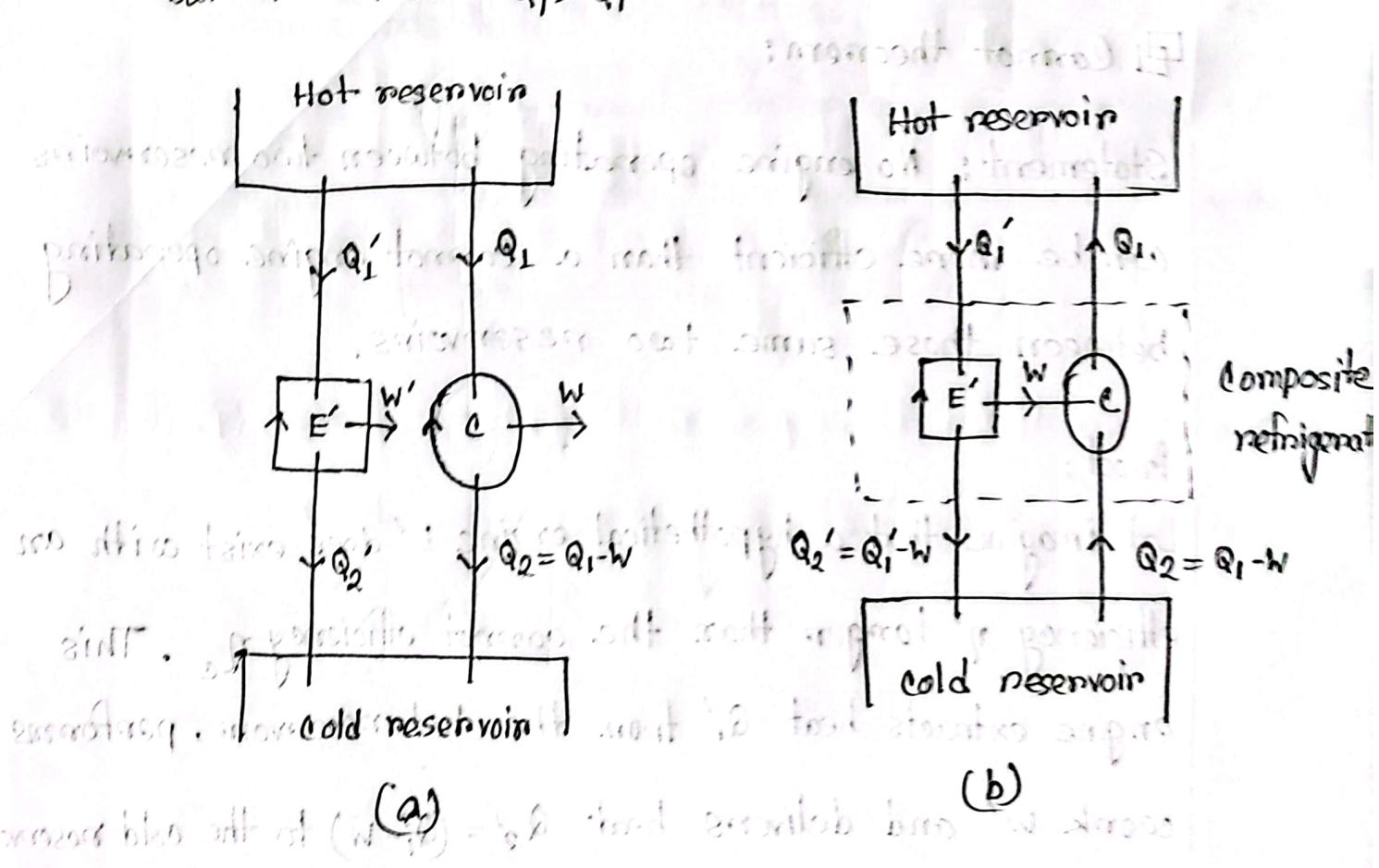
Proof:

Let imagine that a hypothetical engine E' does exist with an efficiency η' larger than the Carnot efficiency η_C . This engine extracts heat Q_1' from the hot reservoir, performs work W' and delivers heat $Q_2' = (Q_1' - W')$ to the cold reservoir.

Now operate a carnot engine, denoted by E and with efficiency η_c , between the same two reservoirs. The carnot engine extracts heat Q_1 , expels Q_2 and delivers work w . Adjust the size of the cycle to make the carnot engine perform the same amount of work as the hypothetical engine E' , so $w' = w$. For the carnot engine $Q_2 = Q_1 - w$. Because the hypothetical engine is assumed to be more efficient than the carnot engine,

$$\frac{W_e'}{Q_1'} > \frac{W}{Q_1}$$

But $w' = w$, so $Q_1 > Q_1'$



A cannot engine is reversible engine, so it may be driven backward as a refrigerator as shown in fig.(b). The hypothetical engine and the cannot refrigerator together act as a composite device, shown by dashed line, which extracts positive heat ($Q_1 - Q'_1$) from the cold reservoir and delivers the same heat to the hot reservoir with no external work being required. But the reservoirs are just large bodies in which the temperature is unchanged upon the addition of heat.

This means that there is a violation of the clausius statement.

Therefore the engine E' cannot exist, and the original assumption that $\eta' > \eta_c$ is incorrect. It is permitted to have $\eta' = \eta_c$ at most. In that case, the composite refrigerator simply refers no net heat for no work which is allowed.

We conclude that, for any real engine,

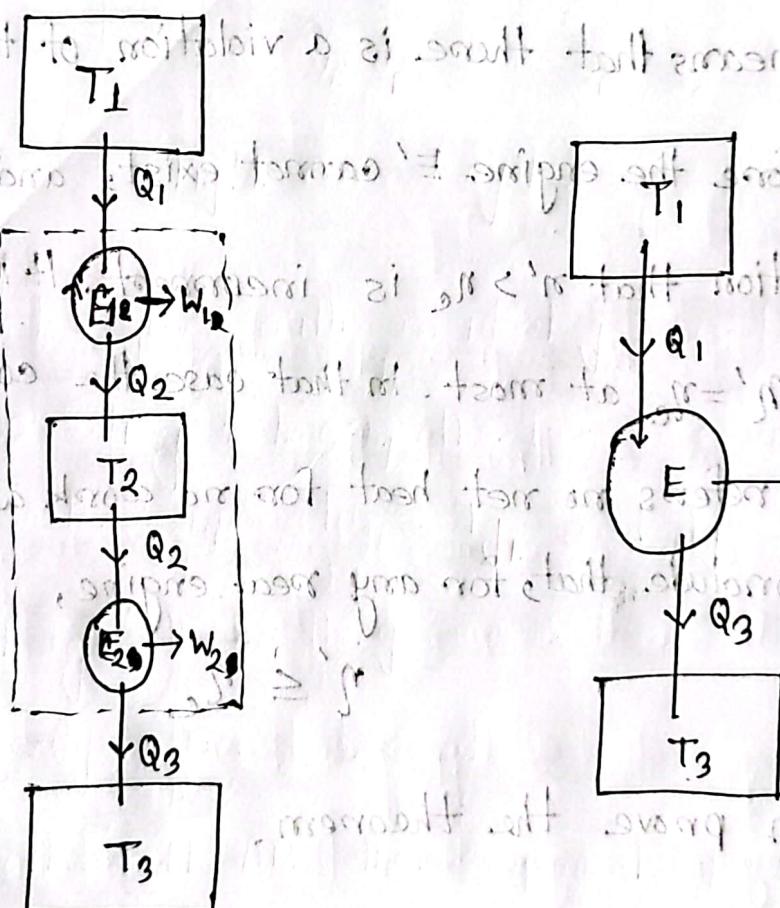
$$\eta' \leq \eta_c$$

which prove the theorem.

Corollary to Carnot's theorem

It follows from Carnot's theorem that "All Carnot engines operating between the same two reservoirs have the same efficiency."

Thermodynamic temperature scale:



From the above figure, E_1 and E_2 are two reversible heat engines and T_1, T_2, T_3 are the temperature limits.

The efficiency for the 1st engine,

$$\eta_1 = 1 - \frac{Q_2}{Q_1} \quad \text{--- (1)}$$

$$\therefore \eta_1 = f(T_1, T_2) \quad \text{--- (2)} \quad [\because \text{working in temperature limit } T_1, T_2]$$

$$\text{Therefore, } 1 - \frac{Q_2}{Q_1} = f(T_1, T_2)$$

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

$$\therefore \frac{Q_1}{Q_2} = \frac{1}{1 - f(T_1, T_2)} = \phi_1(T_1 - T_2)$$

$$\text{Similarly, } \frac{Q_3}{Q_2} = 1 - f(T_2, T_3)$$

$$\therefore \frac{Q_2}{Q_3} = \frac{1}{1 - f(T_2, T_3)} = \phi_2(T_2 - T_3)$$

Now for the engine E_3 (fig. 2) at constant volume and loshi

$$\text{Now, } \frac{Q_1}{Q_2} = \frac{\phi_1(T_1, T_3)}{\phi_2(T_2, T_3)} = \frac{\psi(T_1)}{\psi(T_2)}$$

$\therefore \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ valid only for reversible cycle.

(1) \rightarrow (2) \rightarrow (3)

Equivalence of Thermodynamic temperature scale and ideal gas temperature scale:

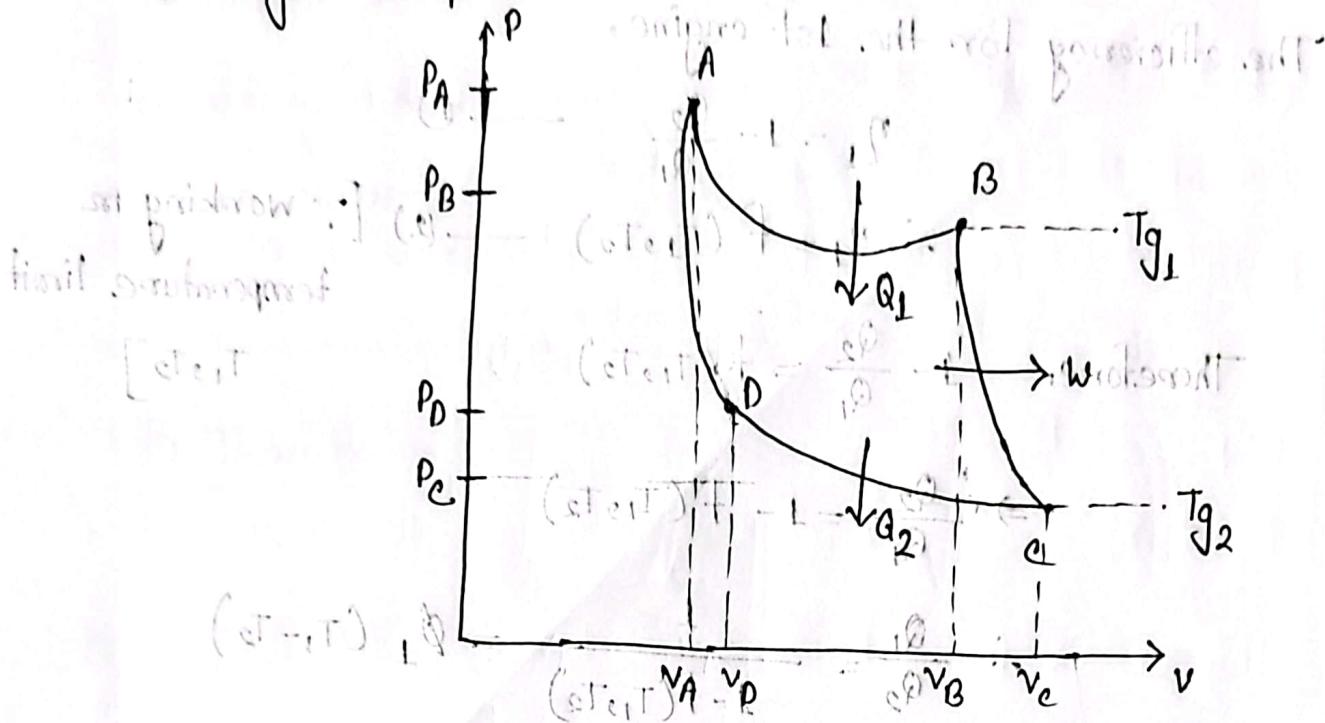


Fig. 1 Carnot cycle

Let a Carnot engine with an ideal gas as the working substance operating between the two reservoirs at the ideal gas scale temperature T_{g1} and T_{g2} .

[The symbol T_g will be the gas scale temperature and T be the thermodynamic temperature.]

For the isothermal AB, the empirical equation of state involving the gas scale temperature T_{g1} is;

$$PV = nRT_{g1} \quad \text{--- (1)}$$

The first law gives for an infinitesimal part of this reversible process

$$dQ = dU + PdV = PdV \quad \text{--- (2)} \quad [\text{At } T=\text{constant}]$$

The heat Q_1 entering the engine in this portion of the cycle is,

$$Q_1 = \int_{V_1}^{V_2} P dV = nRTg_1 \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$Q_1 = nRTg_1 \ln\left(\frac{V_2}{V_1}\right) \quad \text{--- (3)}$$

Q_1 is positive and $V_2 > V_1$ which is consistent with the idea that heat enters the engine in this portion of the cycle.

Similarly, the heat entering the engine along the CD Isotherm part of the cycle is $nRTg_2 \ln\left(\frac{V_4}{V_3}\right)$. This is negative if $V_4 > V_3$ which means that heat flows out of the engine.

However, positive Q_2 has been defined as the heat flows out of the engine,

$$Q_2 = -nRTg_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$\therefore Q_2 = nRTg_2 \ln\left(\frac{V_3}{V_4}\right) \quad \text{--- (4)}$$

Dividing equation (3) by (4)

$$\text{Divide by } T_1 \text{ from 1st equation} \Rightarrow \frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{Tg_1 \ln(\nu_2/\nu_1)}{Tg_2 \ln(\nu_3/\nu_4)} \quad (5)$$

But DA and BC are adiabatices where $Tg V^{\gamma-1} = \text{constant}$

$$\text{Divide by } v_1 \text{ and } v_2 \text{ from 2nd equation} \Rightarrow Tg_1 v_2^{\gamma-1} = Tg_2 v_3^{\gamma-1} = \text{constant} \quad (6)$$

$$Tg_1 v_1^{\gamma-1} = Tg_2 v_4^{\gamma-1} = \text{constant} \quad (7)$$

Dividing equation (6) by (7)

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

$$\Rightarrow \ln\left(\frac{v_2}{v_1}\right) = \ln\left(\frac{v_3}{v_4}\right) \text{ from dividing eqn 6}$$

Substituting this value in equation (5),

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{Tg_1}{Tg_2}$$

$$\Rightarrow \frac{Tg_1}{T_1} = \frac{Tg_2}{T_2}$$

$$\Rightarrow \frac{Tg}{T} = \text{constant}$$

$$\therefore Tg = \epsilon T.$$

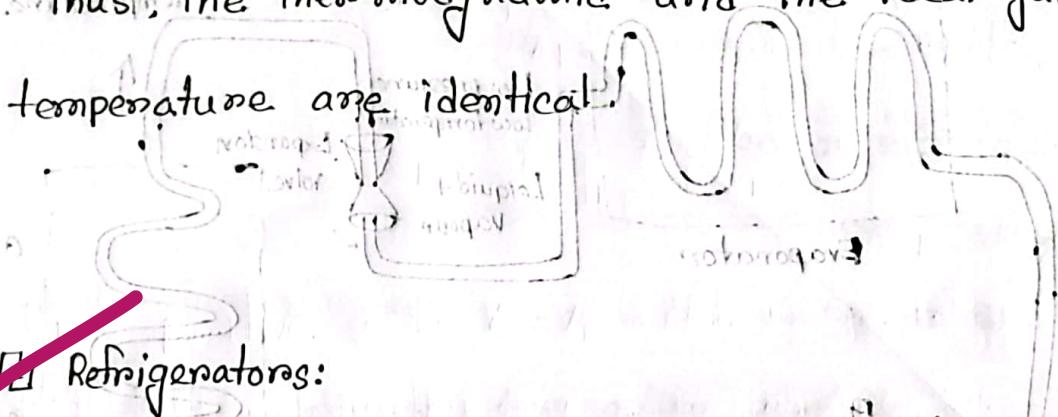
(b) $\nu_1 < \nu_2$ \therefore $Tg_1 < Tg_2$

where ϵ is a constant. Because all temperature scales agree at the fixed point of 273.16K , the constant ϵ must be unity.

$$\therefore T_g = T$$

$\therefore T_g = T$ to maintain pressure

Thus, the thermodynamic and the ideal gas scales of temperature are identical.



Refrigerators:

A refrigerator is a heat engine in which work is done on a refrigerant substance in order to collect energy from a cold region and exhaust it in a higher temperature region.

Explain
Refrigerators have made use of fluorinated

hydrocarbons, which can be forced to

evaporate and then condense by

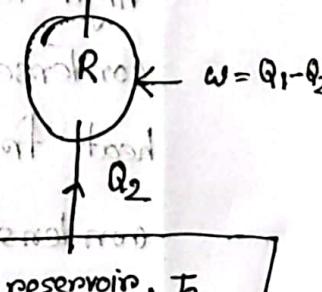
successively lowering and raising the

pressure. It can therefore pump out

energy from cold region to a hotter

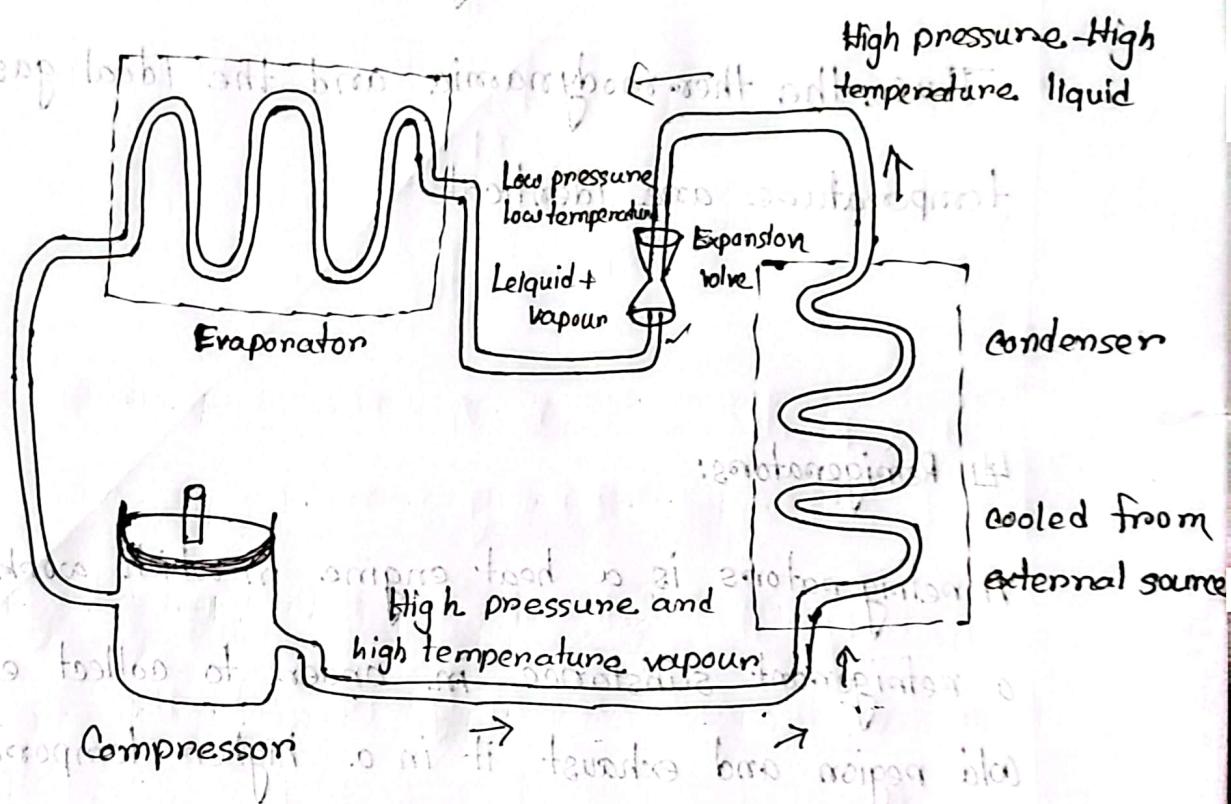
Hot reservoir, T_1

Cold reservoir, T_2



region by extracting the heat of vaporization from the cold region and dumping it in the hotter region outside the refrigerator.

~~Working mechanism of a refrigerator:~~



Firstly in the compressor refrigerent agent (Amonea gas) compressed in the compressor. Thus the gas heat up. Then the high pressure and high temperature gas leave the compressor and entered into the condenser through the connected pipe. The condenser absorbs the heat from the gas and completely converted into liquid. This condenser cooled the gas by external source (surroundings).

This high pressure, high temperature liquid refrigerant agent leave the condenser and pass through the expansion valve by the connected pipe and liquid refrigerant agent expand. Thus the pressure decreases and the temperature falls. Hence the high pressure and high temperature liquid refrigerant will be expanded into low pressure, temperature mixture of liquid and vapour.

Thus we get a mixture of very cold refrigerant agent. Then when this mixture pass through the evaporator coils, it will absorbs all the heat present in the surface of evaporator coils and this refrigerant agent completely turns into low pressure vapour refrigerant. Thus the surroundings of the evaporator becomes cool. Hence the cooling effect of a refrigerator occurs in the evaporator region. After that the vapour again enters into the compressor and the cycle keep repeating over and over again.

~~level~~ Entropy : Entropy is a measure of disorder or randomness of a system.

Entropy is defined as a measure of randomness or disorder of a system.

Entropy is the physical quantity which is always remain constant in an adiabatic process.

If a system at a constant temperature T , accepts or rejects dQ amount of heat, then the entropy change,

$$dS = \frac{dQ}{T}$$

In an adiabatic process, there is no exchange of heat between the system and surroundings. Thus $dQ = 0$.

Therefore entropy change, $dS = \frac{dQ}{dT} = 0$

Hence no change in entropy occurs in an adiabatic process.

It is also defined as single valued function of the thermodynamic variables describing the state of a working substance.

~~E~~ Characteristics of Entropy : (significance)

1. Entropy is a state function.
2. Entropy is a real physical quantity that express the state of matter.
3. The value of entropy depends on the current state of matter, not on the past history of matter.
4. Entropy is a natural quantity whose value is equal to the ratio of heat to absolute temperature ($S = \frac{Q}{T}$)
5. It is a thermal measurement of the object which indicates the direction of heat conduction.
6. It helps to determine the thermodynamic state of an object.
7. Entropy remains constant when the process is reversible in adiabatic process.
8. Entropy increases when the process is irreversible.
9. It can not be felt like temperature and pressure.
10. Due to increase in entropy, unavailable energy increases.
11. The second law of thermodynamics can be stated in terms of entropy of a system.

■ Central equation of thermodynamics:

We have from entropy, heat added at constant T

$$\text{heat added} = \text{entropy change} \times T \quad \Rightarrow \quad dQ = TdS$$

Also we have, $dW = PdV$ (at constant P)

Now from the 1st law of thermodynamics, heat addition

$$dQ = dU + dW$$

$$\Rightarrow TdS = dU + PdV$$

$$(\frac{\partial}{\partial T} = 1) \Rightarrow dU = PdS - PdV \quad \text{of heat to system}$$

This is the central equation of thermodynamics at H

■ Path independence of entropy:

The change in entropy between two states does not depend on the path chosen for the transition.

any two states does not depend on the path chosen for the transition.

Let us suppose an object goes from state A to state B

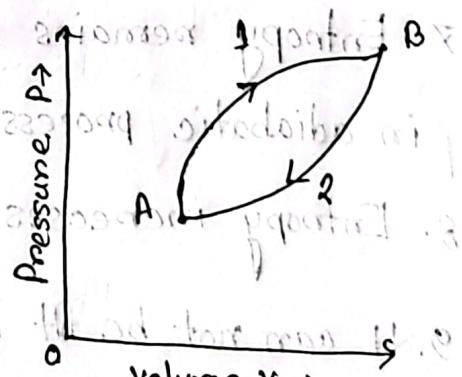
in route 1 and return to A in route 2.

Let us suppose an object goes from state A to state B

in route 1 and return to A in route 2.

Let us suppose an object goes from state A to state B

in route 1 and return to A in route 2.



\therefore The change in entropy for complete change,

$$= \int_A^B (ds)_1 + \int_B^A (ds)_2$$

As the process is reversible. For this cycle the net change of entropy,

$$\int_A^B (ds)_1 + \int_B^A (ds)_2 = 0$$

$$\Rightarrow \int_A^B (ds)_1 = - \int_B^A (ds)_2$$

$$\Rightarrow \int_A^B (ds)_1 = \int_A^B (ds)_2$$

From the above equation, the change in entropy is the same whether the path 1 or 2 is used to go from state A to state B. This change depends only on the initial and final state of the object.

$$S_B - S_A = \int_A^B ds = \int_A^B \frac{dQ}{T}$$

Reversible part of second law:

Clausius theorem:

Let us consider AB is a reversible cycle. Let us divide the cycle into several smaller cycles.

Let us consider some point A_1, A_2, A_3, A_4 on the cycle. Then with the help

of these points construct adiabatic line A_1b_1, A_2b_2, A_3b_3 and A_4b_4 and also isothermal line a_1b_1, a_2b_2, a_3b_3 and c_1A_2, c_2A_3, c_3A_4 .

We know that the change of entropy in reversible process remains constant.

Now consider every small cycle absorbs dQ_1 heat at T_1

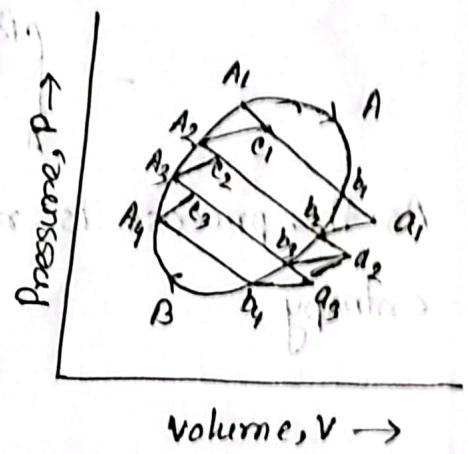
temperature and rejects dQ_2 heat at T_2 .

$$\therefore \frac{dQ_1}{T_1} = \frac{dQ_2}{T_2}$$

$$\Rightarrow \frac{dQ_1}{T_1} - \frac{dQ_2}{T_2} = 0 \quad \text{--- (1)}$$

If the absorbed heat is taken as positive and rejected heat as negative. Then,

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$



Here, $\frac{dQ_1}{T_1}$ indicates the increase in entropy at T_1 temp. and

$\frac{dQ_2}{T_2}$ indicates the decrease in entropy at T_2 temp.

This is applicable for every cycles. Adding all its sums,

$$\sum \frac{Q}{T} = 0$$

$$\sum \frac{\Delta Q_i}{T_i} = 0 \text{ i.e. } \int \frac{dQ}{T} = 0$$

$$\sum ds = 0$$

$$S_f - S_i = 0$$

Thus the clausius theorem can be state,

"Entropy is constant in any reversible process."

$$\text{i.e. } \sum \frac{Q}{T} = 0$$

¶ Inversible part of second law:

(Clausius inequality)

Let us consider an irreversible cycle

in which a high-temperature reservoir

at T_1 supplying a small quantity of

heat dQ_1 to an reversible engine R.

Engine R rejects a small amount of

High temperature
reservoir, at T_1

$$dQ_1$$

R

$$dQ$$

I
 T
 T'

$$dw$$

heat dQ at temperature T that is supplied to the irreversible engine I. Engine I does a small amount of work dW during an irreversible cycle, so the combined system of engine R and engine I also performs an irreversible cycle.

The net work of the combined system, according to the 1st law, equals to $\oint dQ_1$. But the net work cannot be positive according to the Kelvin Plank statement of the second law.

So $\oint dQ_1$ can not be positive. Moreover if $\oint dQ$ equals zero, then, at the end of the cycle, engine I and its surroundings have returned to their original state. So we conclude,

$$\oint dQ_1 < 0 \quad (1)$$

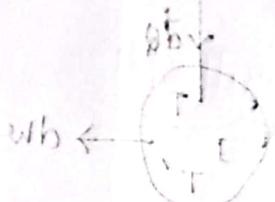
That is engine I generates heat that flows out of the system.

Now from the definition of the thermodynamic temperature scale,

$$\frac{dQ_1}{T_1} = -\frac{dQ}{T}$$

Integrating around a cycle,

$$\oint_R \frac{dQ_1}{T_1} = \oint_R -\frac{dQ}{T}$$



Now T_1 is constant, so, heat lost from I will be $\int_I \frac{dQ}{T}$

difference of areas $\Rightarrow \int_I \frac{dQ}{T} = \frac{1}{T_1} \int_R dQ$, — (2)

Conformations equivalent R top and R bottom (parallel paths)

The heat dQ rejected from R is absorbed by I , so; $-dQ_R = dQ_I$

Putting these values in (1),

$$\int_I \frac{dQ}{T} = \frac{1}{T_1} \int_R dQ,$$
$$\Rightarrow T_1 \int_I \frac{dQ}{T} = \int_R dQ < 0 \quad [\text{from equation (1)}]$$

Since $T_1 > 0$, the result is \Rightarrow always zero, which is not true.

$$\int_I \frac{dQ}{T} < 0 \quad \rightarrow (3) \quad [\text{Irreversible}]$$

of processes with respect to balance sheet with ΔH not

The equation provides the second part of the second law
and is known as Clausius inequality.

The Clausius inequality states,

For any internally irreversible cycle, the closed integral

$\int_I \frac{dQ}{T}$ of the ratio of the heat absorbed by a system to

the temperature at which the heat is received is always

Less than zero.

So it is seen that the closed integral is less than zero for an irreversible cycle and equal to zero for reversible cycle. Combining these two we get clausius mathematical statement of the second law of thermodynamics.

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

~~[Relationships exist]~~ Entropy change for an ideal gas:

Let us consider, one mole of ideal gas, occupying a volume v at pressure P and temperature T .

Let dQ be the heat supplied to the gas, then according to

first law of thermodynamics, we have,

$$dQ = dU + dW \quad \text{(1)}$$

Let C_v be the specific heat at constant volume. dT be the rise of temp. and dv be the change in volume. Then,

$$dU = C_v dT$$

$$dW = -P dv$$

Putting this value in equation (1),

$$dQ = C_v dT + P dV \quad \text{--- (2)}$$

If s is the entropy per unit mass of the gas, then

$$ds = \int \frac{dQ}{T} \quad \text{--- (3)}$$

$$\Rightarrow ds = \int \frac{1}{T} (C_v dT + P dV)$$

$$\Rightarrow ds = \int C_v \frac{dT}{T} + \int \frac{P}{T} dV \quad \text{--- (3)}$$

For an ideal gas,

$$PV = RT$$

$$\Rightarrow \frac{P}{T} = \frac{R}{V}$$

Putting this in equation (3)

$$ds = \int_{T_1}^{T_2} C_v \frac{dT}{T} + \int_{V_1}^{V_2} \frac{R}{V} dV$$

$$= C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{Integrating, } S_f - S_i = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$\Rightarrow ds = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{--- (4)}$$

This is the entropy for ideal gas in term of temperature and volume.

$$\frac{V_2}{V_1} = \left(\frac{T_2}{T_1} \right)^{\frac{C_v}{R}}$$

* Entropy for ideal gas in term of temperature and pressure,

From 1st law of thermodynamics,

$$dQ = dU + dW \quad \text{--- (1)}$$

Let C_p is the specific heat at constant pressure and dT is the raise in temperature and dv is the change in volume,

$$dU = C_p dT \quad \text{and}$$

$$dW = P dv$$

From (1),

$$dQ = C_p dT + P dv \quad \text{--- (2)}$$

If s is the entropy per unit mass of the gas,

$$ds = \int \frac{dQ}{T}$$

$$\Rightarrow ds = \int \left(\frac{C_p dT}{T} + \frac{P dv}{T} \right) \quad \text{--- (3)}$$

For ideal gas, $PV = RT$

$$\Rightarrow P = \frac{RT}{V}$$

Putting these value in equation (3),

$$ds = C_p \int_{T_1}^{T_2} \frac{dT}{T} + \int_{V_1}^{V_2} \frac{RT}{V} \frac{dV}{T}$$

$$\Rightarrow ds = C_p \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow \Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

Again we know,

$$P_1 V_1 = P_2 V_2$$

$$\Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore \Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

(1) —

$$\left(\frac{R}{C_p} + \frac{R}{C_v} \right) = \frac{R}{C_p}$$

The equations are,

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad (1)$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \quad (2)$$

In isothermal process : $T_1 = T_2$

$$\therefore \Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}$$

In isochoric process : $V_1 = V_2$

$$\Delta S = C_v \ln \frac{T_2}{T_1}$$

In isobaric process : $P_1 = P_2$

$$\Delta S = C_p \ln \frac{T_2}{T_1} + \left(\frac{R}{C_p} + \frac{R}{C_v} \right)$$

~~The principle of increasing of entropy:~~

As entropy is terms of pressure and volume,

For an ideal gas,

$$\begin{aligned} pV &= RT \\ \Rightarrow T &= \frac{pV}{R} \\ \therefore dT &= \frac{pdV + Vdp}{R} \end{aligned}$$

— (1)

First law of thermodynamic,

$$dQ = dU + dW$$

$$\Rightarrow dQ = C_v dT + PdV$$

$$\text{Entropy } ds = \int \frac{dQ}{T} = \int \frac{C_v dT + PdV}{T}$$

$$\Rightarrow ds = \int \frac{1}{T} (C_v dT + PdV) = \Delta S$$

$$= \int C_v \frac{PdV + Vdp}{RT} + \int \frac{PdV}{T}$$

$$= \int C_v \frac{PdV + Vdp}{PV} + \int \frac{PdV}{R PV}$$

$$= \int C_v \left(\frac{dp}{p} + \frac{dv}{v} \right) + \int R \frac{dv}{v}$$

$$\begin{aligned}
 &= \int C_V \left(\frac{dp}{v} + \frac{dv}{p} \right) + \int (C_P - C_V) \frac{dv}{v} \quad [R = C_P - C_V] \\
 &= \int C_V \frac{dv}{v} + \int C_V \frac{dp}{p} + \int C_P \frac{dv}{v} - \int C_V \frac{dv}{v} \\
 &= C_V \int \frac{dp}{p} + C_P \int \frac{dv}{v}
 \end{aligned}$$

$\therefore \Delta S = C_V \ln \frac{P_2}{P_1} + C_P \ln \frac{V_2}{V_1}$

~~It corresponds to the first law of thermodynamics~~

~~Principle of increase of entropy :~~

It states that for any process the total change in entropy of a system together with its enclosing adiabatic surroundings is always greater than or equal to zero.

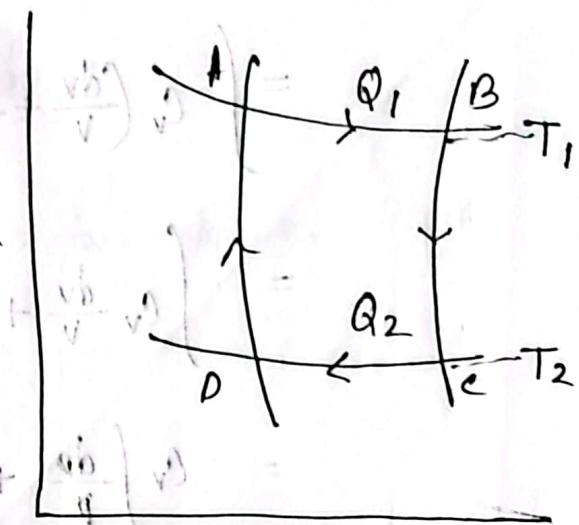
1. In reversible process, the entropy of the system remains constant $\oint dS = 0$

Let us consider ABCD represents the carnot's reversible cycle, In Fig. 1 for an ideal gas formed by two isotherms

isothermal diagram i.e; AB at temp.

T_1 and CD at temperature T_2

and two adiabatic diagram
BC and DA.



During Carnot cycle ABCD, an

amount of heat Q_1 is absorbed in

going from A to B at constant temp. T_1 , and an amount

of heat Q_2 is rejected at constant temperature T_2 .

The change in entropy of the system,

$$\text{of entropy } ds = \frac{dQ}{T}$$

The increase in entropy of the isothermal expansion AB is,

$$\int_A^B ds = + \frac{Q_1}{T_1}$$

The decrease in entropy of the isothermal compression

CD is,

$$\int_C^D ds = - \frac{Q_2}{T_2}$$

In adiabatic process, $ds = \frac{dQ}{T} = 0$ at slope

Therefore, $\int_B^C dS = 0$ and $\int_D^A dS = 0$

Thus, the net gain in entropy of the working substance in the whole cycle ABCDA is,

$$\begin{aligned} \oint dS &= \int_A^B dS + \int_B^C dS + \int_C^D dS + \int_D^A dS \\ &= \frac{Q_1}{T_1} + 0 - \frac{Q_2}{T_2} + 0 \\ \Rightarrow \oint dS &= \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \quad \text{--- (1)} \end{aligned}$$

But for a reversible Carnot cycle,

Substituting this in equation (1)

$$\oint dS = \frac{Q_1}{T_1} - \frac{Q_1}{T_1} = 0$$

Thus in reversible process, the entropy of the system remains unchanged or remains constant. Total change in entropy is always zero.

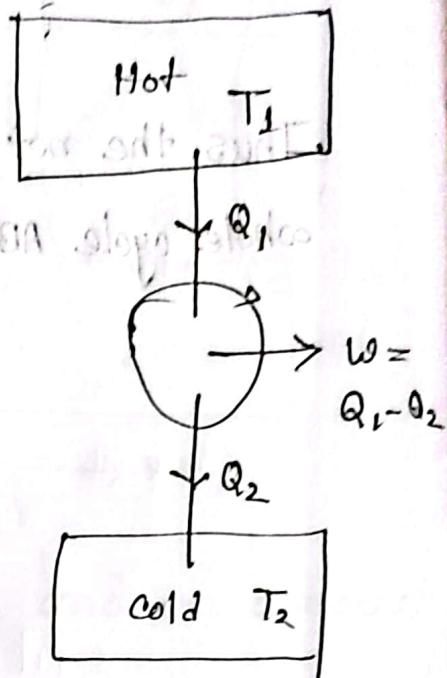
(ii) Irreversible process, $dS > 0$

Let us consider, an engine performing irreversible cycle of changes in which the working substance absorbs heat

Q_1 at temp. T_1 from source and rejects heat Q_2 to the sink at temp. T_2 .

Efficiency,

$$\eta_{\text{irr}} = \frac{w}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$



But according to Carnot theorem, the efficiency is less than that of a reversible cycle engine working between the same two temp. T_1 and T_2 for which efficiency is given by,

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

From Carnot theorem we know,

$\eta_{\text{rev}} > \eta_{\text{irr}}$ or $1 - \frac{T_2}{T_1} > 1 - \frac{Q_2}{Q_1}$

$$\Rightarrow \frac{Q_2}{Q_1} > \frac{T_2}{T_1}$$

$$\rightarrow \frac{Q_2}{T_2} > \frac{Q_1}{T_1}$$

$$\Rightarrow \frac{Q_2}{T_2} - \frac{Q_1}{T_1} > 0$$

$$\Rightarrow dS > 0$$

Considering the whole system, the source loses (-ve sign) the entropy by amount $\frac{Q_1}{T_1}$ and the sink gains (+ve sign) an entropy

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

Therefore, the net change in entropy for the whole system is

$$\left(\frac{Q_2}{T_2} - \frac{Q_1}{T_1} \right)$$

which is clearly greater than zero. i.e; positive.
Thus there is an increase in entropy of the system during an irreversible process. Combined this two statement of

the reversible and irreversible,

$$dS \geq 0$$

This is the principle of increase of entropy.

Start of following is in SA until statements

of substance in contact w/T

~~Q~~ Entropy temperature diagram:

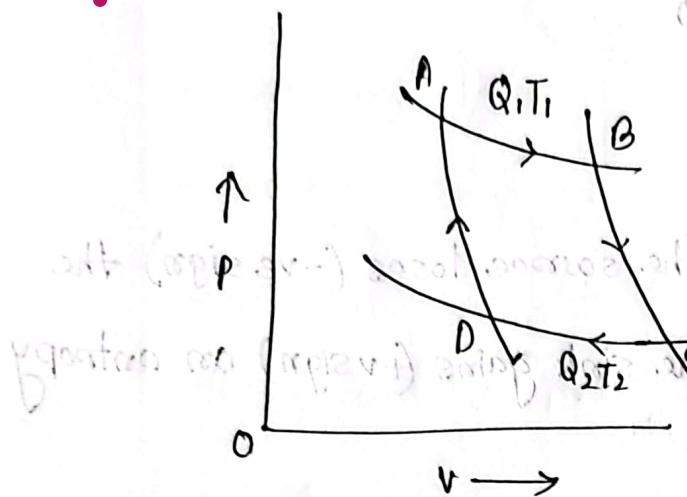


Fig. 1

at isotherm T_1 heat added Q_1 , entropy change ΔS_1 . At isotherm T_2 heat released $-Q_2$, entropy change ΔS_2

Let us consider the Carnot cycle ABCDA, in fig. 1. A Carnot reversible cycle is shown on p-v diagram. It is composed of two isotherms AB and CD at constant tem. T_1 and T_2 respectively.

On the T-S curve, in fig. 2, the isothermal curves are shown by two straight lines AB and CD parallel to S-axis, and the adiabatic curves are shown by the straight line BC and DA parallel to T-axis. The resulting T-S diagram is rectangle ABCD.

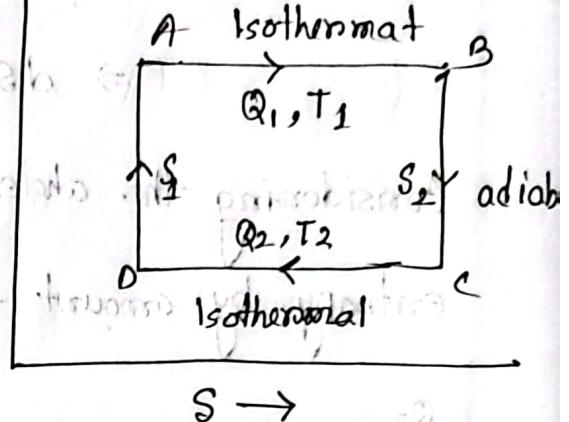


Fig. 2

at isotherm T_1 heat added Q_1 , entropy change ΔS_1 . At isotherm T_2 heat released $-Q_2$, entropy change ΔS_2

Let S_1 be the entropy of the working substance in state A and S_2 is state B, Q_1 be the absorbed heat along AB.

i.e during isothermal expansion at constant temperature

T_1 and Q_2 is the heat rejected in the isothermal compression at constant temperature at T_2 along CD.

Then gain in entropy along AB,

$$\int_A^B dS = \frac{Q_1}{T_1}$$

$$\Rightarrow S_B - S_A = \frac{Q_1}{T_1}$$

$$\Rightarrow Q_1 = T_1 (S_B - S_A) \quad \text{--- (1)}$$

Along CD,

$$\int_C^D dS = -\frac{Q_2}{T_2}$$

$$\Rightarrow S_D - S_C = -\frac{Q_2}{T_2}$$

$$\Rightarrow Q_2 = (S_B - S_A) T_2 \quad \left[\because S_C - S_D = S_B - S_A \right] \quad \text{--- (2)}$$

For adiabatic the change in entropy is zero.

$$\int_B^C dS = 0 \quad \text{and} \quad \int_D^A dS = 0$$

A state of equilibrium will be reached at 12th

From equation (1) and (2),

• QA greater than QB and 12th state is at B from
enthalpy diagram due to more energy present in B

$$Q_1 - Q_2 = T_1 (S_B - S_A) - T_2 (S_B - S_A)$$

$$\text{from left side of enthalpy diagram} = (T_1 - T_2)(S_2 + S_1) \quad [S_B = S_2]$$

$$\text{QA greater than QB due to more energy present in A} \quad [S_A = S_1]$$

The quantity $Q_1 - Q_2$ represents the external work done

in the cycle and $(T_1 - T_2)(S_2 + S_1)$ is the area of rectangle of T-S diagram

Thus the area of the rectangle on the T-S diagram represents the external work done in a reversible Carnot cycle.

$$[a^2 - b^2 = (a+b)(a-b)] \quad gT(a^2 - b^2) = gP$$

area of figure in square unit is given by

