28

(2+3)

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Chapter No. 26

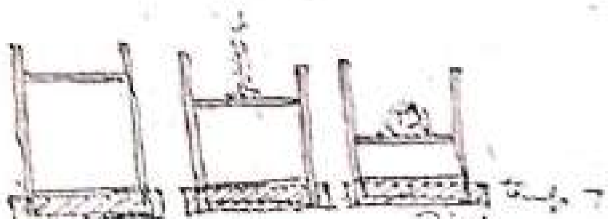
Entropy And The Second Law Of Thermodynamics

Q. What are reversible and irreversible processes?

Ch (25) MCQ

Reversible Process

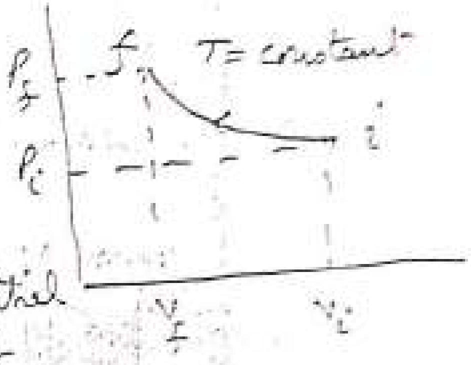
Consider n moles of a ideal gas confined in a cylinder fitted with a piston and walls insulating with conducting base. (assumed to be frictionless)



The initial state (state i) has well defined temperature, volume and pressure. The cylinder is placed on a source at constant temperature T. We first drop a few grains of sand on the piston due to which the volume will reduce a little and the temperature will tend to rise. But it is a very small change, therefore the system almost remains in the thermal equilibrium with the reservoir at constant temperature T, because the excess of heat (small amount of heat) will be transferred to the reservoir. If a few more grains of sand are dropped on the piston, then the volume will reduce further

By many repetitions of this procedure, the volume is reduced by one-half finally. Each time a small amount of heat is transfered to the reservoir, keeping the system in thermal equilibrium and its temperature T remains constant.

This is a reversible process which may be defined as.



"A reversible process is one that by a differential change in the environment, can be made to retrace its path."

A reversible process is always a slow process. In this case it is isothermal process also. This process can be carried out from state i to state f or from state f to state i slowly keeping temperature constant, as shown in PV diagram. This is an ideal process, because we have ~~consider~~ ignored friction and other ~~heat-losses~~. An adiabatic process may also be a reversible process, if the cylinder is placed on an insulating stand and the process is carried out from state i to state f very slowly, which can be retraced also.

Quasi-Static Process. It is a process which is carried out slowly enough

Q. Discuss heat engine and the second law of thermodynamics.

<u>Heat Engine</u>. A heat engine is device which can convert heat energy into useful work.

An ideal gas cylinder placed on a thermal reservoir at temperature T can serve as a heat engine (for example). When the weight from the piston is decreased and the gas is allowed to expand then at constant temperature T, then some heat energy is absorbed by the gas which is converted into work which is done on the environment by the gas. But such engine cannot work for indefinitely because the operation of the engine will be finished when the piston reaches to the top of the cylinder.

The sign conventions which are used for heat and work.

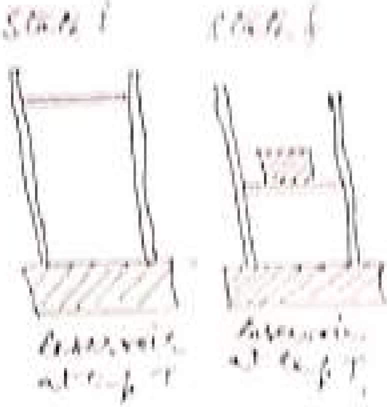
i. Heat entering the system is considered to be positive; heat leaving a system is considered to be negative.

ii. Work done on a system, corresponding to a decrease in volume, is considered to be positive and work done on the system will be negative when volume of the system increases.

During expansion work done is -ve
During compression work done is +ve

iii. Work done in a cyclical process is negative if cycle is done in a clockwise sense on a PV diagram and positive so that the system passes through a continuous sequence of equilibrium state. A quasi-static process may or may not be reversible.

Irreversible Process



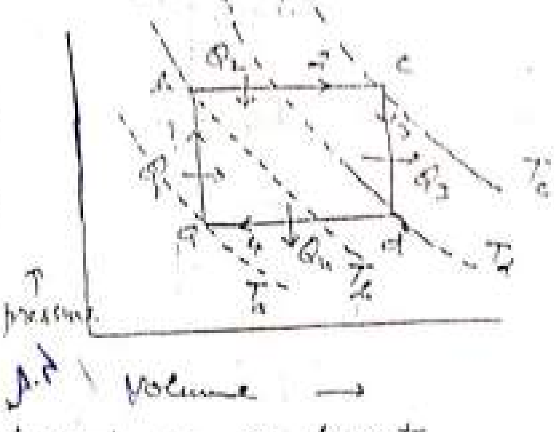
Let 'n' moles of a gas are enclosed in a cylinder fitted with a piston. The piston and walls are insulating while the base is conducting. The cylinder is placed on a reservoir at constant temperature T. The initial state (state i) is well defined. Let the gas is compressed suddenly by putting the load on the piston. Then the equilibrium state of the gas is disturbed, because its volume is reduced by one-half while its pressure and temperature are increased. This intermediate state is a state of non-equilibrium state, because the temperature and pressure are not well defined and it will take a time to reach at the final equilibrium state (state f). The intermediate state cannot be represented by PV diagram. Also this sudden process cannot be retraced, therefore this is an irreversible process. All the real processes are irreversible due to friction and other heat losses or dissipative effects.

If the cycle is
done counterclockwise

Heat Engine (operating in a cycle)

A useful heat engine is that which is operating in a cycle. A cycle or cyclical process may consists of different steps during which the temperature, volume and pressure may change, but after one cycle the engine will be back to its initial state.
Let the cycle of a heat engine consists of the following four steps

Step 1 (ab)
(Constant-Volume Process)
A cylinder filled with gas and fitted with a piston may serve as a heat engine. Let such



a heat engine is placed on a heat reservoir so that its temperature increases but some load is added on the piston to keep the volume constant. During this process Q_1 heat is absorbed while the temperature and pressure are increased, which is represented by ab.

Step 2 (bc)
(Constant-Pressure Process). Let the engine is placed on a heat reservoir and

The gas is allowed to expand at constant pressure. During this process heat 'Q_2' is absorbed by the engine. while the volume and temp of the gas increase. This process is represented by the curve bc

Step 3. (cd) (Constant-Volume Process). Let the temperature of the reservoir is decreased also ~~the~~ some weight from the piston is also removed so that the volume remains constant. During this process heat 'Q_3' is removed from the system while its temperature and pressure decrease. This process is represented by (cd) in PV diagram.

Step 4 (da) (Constant-Pressure Process) The temperature of the reservoir is decreased and 'Q_4' heat is removed from the system. The volume and temperature of the system decrease at constant pressure. This process is represented by (da) curve in PV diagram.

The dotted lines are the isotherms. After the completion of four steps the engine is back to its initial state. During one cycle heat energies Q_1 and Q_2 are absorbed while heat energies Q_3 and Q_4 are rejected by the system. As the system is at its initial state therefore there is no change

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The internal energy of the system.

or

$\Delta E_{int} = 0$

According to first law of thermodynamics

$\Delta E = Q + W$

$0 = Q + W$ $\quad 0 = Q + W$,

or $Q = -W$.

As the cyclical process is clockwise, therefore negative work is done on the system; and 'Q' is the net heat absorbed by the system. In other words 'Q' heat is converted into useful work 'W' by the heat engine.

But

Heat absorbed $= Q_{in} = Q_1 + Q_2$

Heat rejected $= Q_{out} = Q_3 + Q_4$

Net heat absorbed by the heat engine in terms of magnitude (which is equal to work done by the engine)

$|W| = |Q| = |Q_{in}| - |Q_{out}|$

The efficiency of the heat engine (in one cycle) is defined as the net amount of work done $|W|$ on the environment during the cycle divided by the heat input $|Q_{in}|$.

or

$$\boxed{e = \frac{|W|}{|Q_{in}|}} = \frac{|Q_{in}| - |Q_{out}|}{|Q_{in}|} = 1 - \frac{|Q_{out}|}{|Q_{in}|}$$

Therefore the efficiency of a real heat engine is always less than 1 or 100%.

If $Q_{out} = 0$, then $e = 1$ or 100%.

Therefore the efficiency of a perfect heat engine is 1 or 100%, which is impossible.

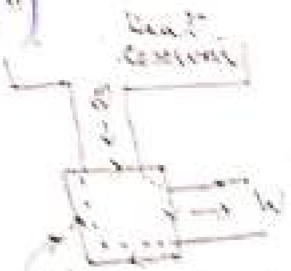
Second Law of Thermodynamics

The Kelvin statement of second law of thermodynamics is "It is not possible in a cyclical process to convert heat entirely into work, with no other change taking place". Here "no other change taking place" is the exhaust heat or heat rejected by the heat engine (Q_{out}). (According to second law of thermodynamics, there is no heat engine working in a cyclical process has exhaust heat (Q_{out}) equal to zero, and having efficiency equal to 1 or 100%. Therefore the second law which is sometimes called the Kelvin-Planck form, states that "there are no perfect heat engine.")

For perfect heat engine

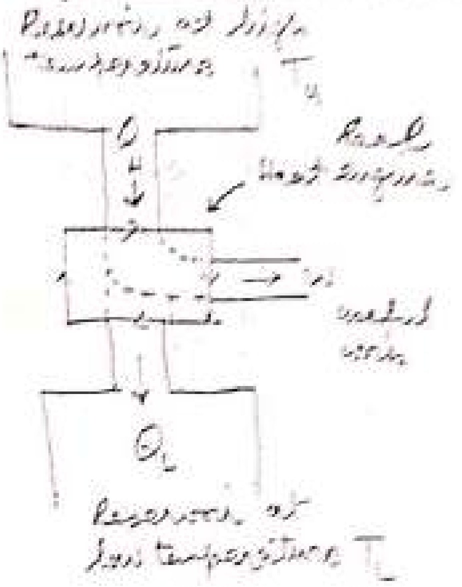
$W = -Q$ or $Q = -W$

which is not possible because all the heat taken from a reservoir cannot be converted into useful work.



Perfect Heat engine

According to second law of thermodynamics a heat engine can convert only a part of heat energy into useful work as shown in the Fig.



Q_H is the heat absorbed by the heat engine from a reservoir at high temperature T_H and Q_L is the heat rejected by it to a reservoir at low temperature T_L. Therefore the useful work done W by the heat engine in a cyclical process is

$$W = |Q_H| - |Q_L|$$

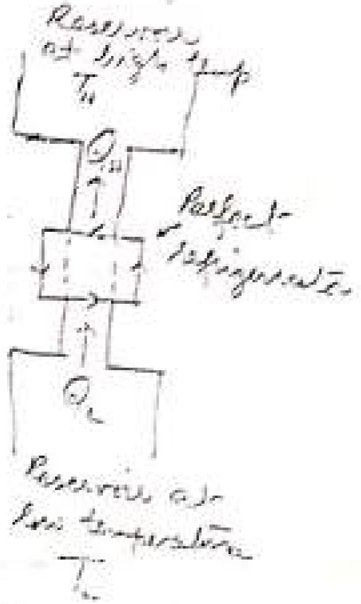
Here $|Q_L|$ cannot be equal to zero for a real heat engine. The cycle involves a series of operations performed on a "working substance". For example, in a power plant, the "working substance" is water. Here Q_H is heat absorbed by the water when it is converted into steam, and Q_L is the heat rejected by it when it is converted into water again after doing useful work.

Q. Discuss refrigerator and second law of thermodynamics.

Refrigerator and the Second Law Thermodynamics

A refrigerator is basically a heat engine operating in the reverse direction.

Let Q_L is the heat extracted by the refrigerator from low-temperature reservoir and Q_H is the heat given to the high-temperature reservoir.



In case of a perfect refrigerator, the heat energy from cold body will be transferred to hot body without any expenditure of energy or

$$|Q_L| = |Q_H|$$

But this is against the fact, because heat energy cannot flow by itself from low-temperature reservoir to high-temperature reservoir. Therefore a perfect refrigerator is impossible.

For real refrigerator $Q_H > Q_L$. It means that some external work must be done on the refrigerator then it will be able to transfer Q_L heat from low-temperature reservoir to high-temperature reservoir.

total heat
... to the high-temperature reservoir is Q_H, which is given by

$$|Q_H| = |Q_L| + |W| \quad \text{or} \quad |W| = |Q_H| - |Q_L|$$

The coefficient of performance K of refrigerator is given by

$$K = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

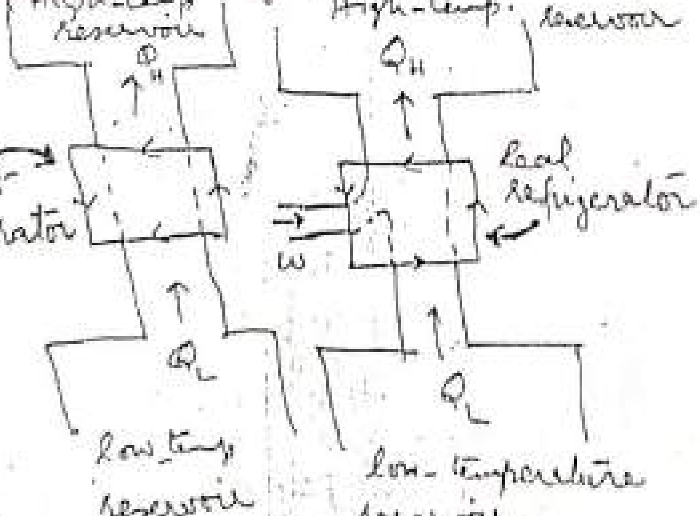
Clausius Statement of Second law of Thermodynamics

The alternate statement of second law of thermodynamics which is called Clausius statement is

"It is not possible in a cyclical process for heat to flow from one body to another body at higher temperature, with no other change taking place"

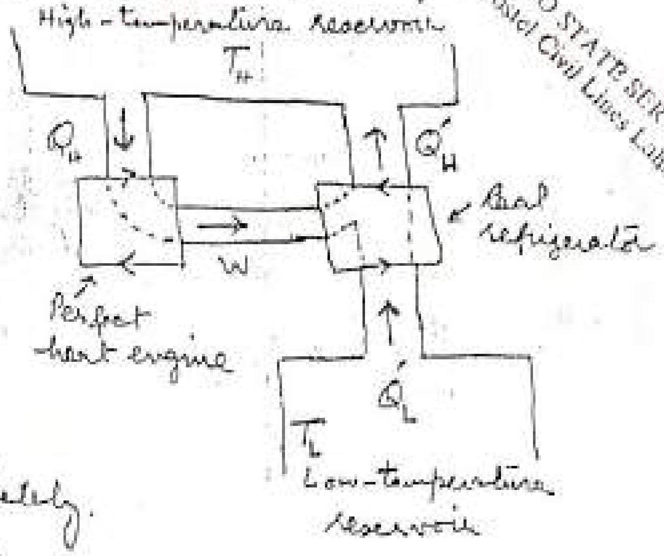
OR "Heat cannot flow from a colder body to a hotter body without the expenditure of energy"

If it is desired to transfer heat from low-temperature reservoir to high temperature reservoir, then some external work W must be done on the engine (refrigerator)



Q. Discuss the equivalence of the Clausius and Kelvin-Planck Statements.

Equivalence of Two Statements



Consider a perfect heat engine which takes Q_H heat from a high-temperature reservoir and converts it into useful work W completely, which is against the Kelvin-Planck form of second law of Thermodynamics.

Therefore $|Q_H| = |W|$

Let this work done W is applied to derive a real refrigerator which takes Q'_L heat from a low-temperature reservoir and transfers $(Q'_L + W)$ heat to the high-temperature reservoir, therefore total heat given to high-temperature reservoir is

$$|Q'_H| = |Q'_L| + |W|.$$

The perfect heat and the real-refrigerator interacting with each other, therefore this combination may be regarded as a single device. Therefore the heat Q_H is taken out and Q'_H is the heat given to the high-temperature reservoir by this single device.

Therefore the net heat given to the high-temperature reservoir is

$$= |Q_H'| - |Q_H| \quad --- \text{I}$$

But $|Q_H'| = |Q_L'| + |W|$ and $|Q_H| = |W|$

Putting these values in Eq I, ~~we get~~, "

The net heat given to the high-temperature reservoir is

$$= |Q_L'| + |W| - |W|$$

$$= |Q_L'|$$

But the heat taken out from low-temperature reservoir is also $|Q_L'|$. It means that $|Q_L'|$ heat is transferred from low-temperature reservoir to high-temperature reservoir without any external work, which is against the Clausius statement. If a perfect heat engine is built, then as a result a perfect refrigerator is also produced. It means that the violation of Kelvin-Planck statement produces a results which is the violation of Clausius statement. Hence the two statements of second law of thermodynamics are equivalent to each other, because a violation of either statement implies a violation of the other.

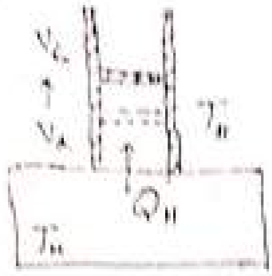
Q. What is carnot engine? Discuss carnot cycle and determine the efficiency of the engine.

Carnot Engine: It is an ideal engine which consists of a cylinder whose walls and piston are insulating while the base is conducting only; and also ideal gas is enclosed in it. This engine is free of from friction and other heat losses.

Carnot Cycle: The carnot engine operates on a particular cycle called carnot cycle which consists of the following four processes.

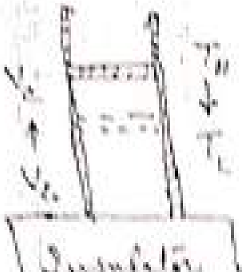
Step I (Process: Isothermal Expansion)

The cylinder is placed on a high temperature reservoir and the gas is allowed to expand at constant temperature T_H while the volume of the gas increases from V_a to V_b and pressure decreases from P_a to P_b. During this isothermal expansion Q_H heat is absorbed by the gas. This process is represented by isotherm ab.



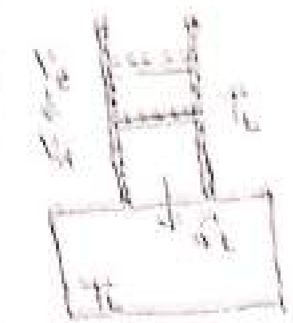
Step II (Process II Adiabatic Expansion)

The cylinder is placed on an insulator and the gas is allowed to expand by decreasing the pressure from P_b to P_c, so that the volume increases from V_b to V_c. During this adiabatic expansion the temperature decreases from T_H to T_L. This process is represented (b-c) adiabatic.



(Process of isothermal compression)

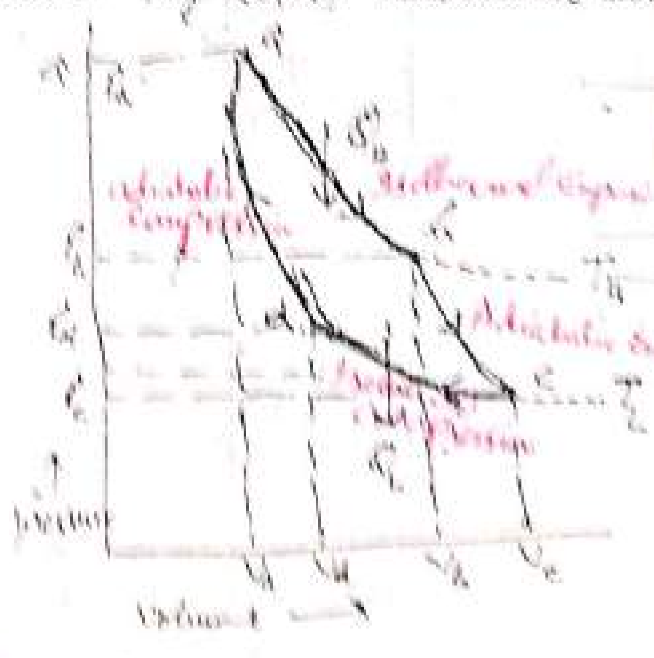
The cylinder is placed on a low conducting material and the gas is compressed slowly by increasing the pressure from P_2 to P_3 while its volume decreases from V_2 to V_3. During this process heat Q_2 is rejected by the gas at constant temperature T_2. This isothermal compression is represented by cd isotherm.



Step IV (Process of adiabatic compression)

The cylinder is placed on an insulating pad and the gas is compressed so that its volume decreases from V_3 to V_1 while pressure increases from P_3 to P_1. During this adiabatic compression the temperature increases from T_2 to T_1. This process is represented by da adiabatic curve.

After these four steps the gas is back at its initial state, therefore one complete cycle has been completed. Therefore there is no change in the internal energy of the gas, $\Delta E = 0$



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The total heat absorbed by the engine is

$$|Q_{in}| = |Q_H|$$

Heat rejected by the engine is

$$|Q_{out}| = |Q_L|$$

Net heat absorbed by the engine is equal to the work done by the engine, therefore

Efficiency

$$|W| = |Q_{in}| - |Q_{out}| = |Q_H| - |Q_L|$$

The efficiency of the Carnot engine is

$$e = \frac{\text{work done}}{\text{Input}} = \frac{|W|}{|Q_{in}|}$$

$$= \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} \quad \text{---- I}$$

This is the equation for the efficiency of the Carnot engine;

Let $|W_1|$ is the work done by the engine during isothermal expansion when 'Q_H' heat is absorbed by the gas, and volume increases from V_a to V_b at constant temp. T_H.

Therefore

$$|W_1| = \int_{V_a}^{V_b} P\,dV = \int_{V_a}^{V_b} nRT_H \frac{dV}{V}$$

$\because PV = nRT$

$\rightarrow P = \frac{nRT}{V}$

$$= nRT_H \ln\left(\frac{V_b}{V_a}\right)$$

Therefore

$$|Q_H| = |W_1| = nRT_H \ln\left(\frac{V_b}{V_a}\right) \quad \text{---- II}$$

As there is no change in the internal energy.

$$\boxed{\Delta E_{int} = 0}$$

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During isothermal compression 'W' is the work on the system when 'Q' heat is rejected by the gas at constant temperature T_L and volume decreases from V_c to V_d, therefore the work done is

$$W_3 = \int_{V_c}^{V_d} P\,dV = \int_{V_c}^{V_d} nRT_L \frac{dV}{V} = nRT_L\left[\ln V_d - \ln V_c\right]$$

As heat is rejected by the gas, therefore

$$-Q_L = W_3$$

or

$$-Q_L = nRT_L\left[\ln V_d - \ln V_c\right]$$

or

$$Q_L = nRT_L\left(\ln V_c - \ln V_d\right)$$

or

$$|Q_L| = nRT_L \ln\left(\frac{V_c}{V_d}\right) \quad \text{---- iii}$$

Dividing Eq iii by Eq ii, we get

$$\frac{|Q_L|}{|Q_H|} = \frac{nRT_L \ln\left(\frac{V_c}{V_d}\right)}{nRT_H \ln\left(\frac{V_b}{V_a}\right)} = \frac{T_L}{T_H}\,\frac{\ln(V_c/V_d)}{\ln(V_b/V_a)} \quad \text{---- iv}$$

For adiabatic processes bc and da, we get

$$T_H V_b^{\gamma-1} = T_L V_c^{\gamma-1} \quad \text{and} \quad T_H V_a^{\gamma-1} = T_L V_d^{\gamma-1}$$

or

$$\frac{T_H}{T_L} = \frac{V_c^{\gamma-1}}{V_b^{\gamma-1}} \qquad \frac{T_H}{T_L} = \frac{V_d^{\gamma-1}}{V_a^{\gamma-1}}$$

Comparing

$$\frac{V_c^{\gamma-1}}{V_b^{\gamma-1}} = \frac{V_d^{\gamma-1}}{V_a^{\gamma-1}}$$

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}$$

or $$\frac{V_c}{V_d} = \frac{V_b}{V_a}$$

Putting these values in Eq IV, we get

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}$$

Putting these values of in Eq V, we get

$$e = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H}$$

or

$$e = \frac{|Q_H| - |Q_L|}{|Q_H|} = \frac{T_H - T_L}{T_H}$$

This are the equations for the efficiency of the carnot engine.

Q Result

Therefore the efficiency of the carnot engine depends only on the temperatures of the two reservoirs between which it operates and not on the working substance. As carnot cycle is reversible therefore carnot engine can be run backward to make a refrigerator. Therefore the coefficient of performance of a carnot refrigerator is

Performance

$K = \frac{Q_L}{W}$

$K = \frac{Q_L}{Q_H - Q_L}$

$$K = \frac{|Q_L|}{|Q_H| - |Q_L|} = \frac{1}{\frac{|Q_H|}{|Q_L|} - 1} \qquad \left[\because \frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L}\right.$$

$$K = \frac{1}{\left(\frac{T_H}{T_L}\right) - 1} = \frac{1}{\frac{T_H - T_L}{T_L}} = \frac{T_L}{T_H - T_L}$$

These are the equations for the coefficient of performance of carnot refrigerator.

RSII

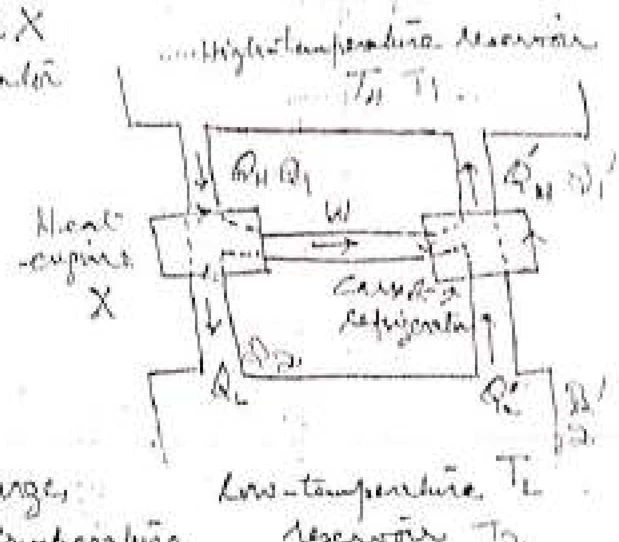
Q11 Carnot theorem and the second law of thermodynamics. CA (Q2) P (17)

Carnot Theorem And Second Law of Thermodynamics.

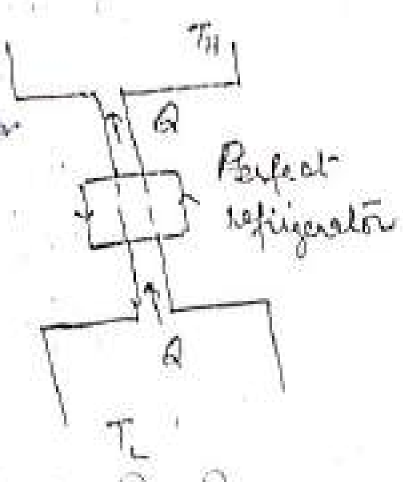
Carnot Theorem may be stated as

"The efficiency of any heat engine operating between two specified temperatures can never exceed the efficiency of a Carnot engine operating between the same two temperatures."

Consider a heat engine X and a carnot refrigerator which are operating between the same two temperatures T_H and T_L.



Let the heat engine X extracts heat Q_H from high temperature reservoir and discharges heat Q_L to the low-temperature reservoir, doing W work in the process. This work W drives the carnot ~~engine~~ refrigerator which extracts Q'_L heat from low-temperature reservoir and discharges Q'_H heat to the high-temperature reservoir.



$\therefore Q'_H = |Q'_L| + W$

Therefore $|W| = |Q_H| - |Q_L|$ $\qquad W = Q_1 - Q_2$

Also $|W| = |Q'_H| - |Q'_L|$. $\qquad W = Q'_1 - Q'_2$

$\qquad Q_1 - Q_2 = Q'_1 - Q'_2$

$\therefore |Q'_H| - |Q'_L| = |Q_H| - |Q_L|$ $\qquad Q'_1 - Q_1 = Q'_2 - Q_2$

$$|Q_H'| - |Q_H| = |Q_L'| - |Q_L|$$

$$Q = |Q_H'| - |Q_H| = |Q_L'| - |Q_L| \quad \ldots \mathrm{I}$$

The efficiency of the heat engine X is

$$\eta_X = \frac{|W|}{|Q_H|} \qquad \eta_X = \frac{|W|}{Q_1}$$

Similarly the efficiency of the Carnot engine is

$$\eta = \frac{|W|}{|Q_H'|} \qquad \eta = \frac{|W|}{Q_1'}$$

Let the efficiency of any heat engine X is greater than that of Carnot engine.

or

$$\eta_X > \eta \quad \ldots \mathrm{II}$$

or

$$\frac{|W|}{|Q_H|} > \frac{|W|}{|Q_H'|} \quad \text{or} \quad \frac{1}{|Q_H|} > \frac{1}{|Q_H'|}$$

or

$$|Q_H'| > |Q_H|$$

Therefore the difference of $|Q_H'|$ and $|Q_H|$ must be positive

or

$$|Q| = |Q_H'| - |Q_H|$$

and

$$|Q| > 0$$

The net heat taken out from the low temperature reservoir is 'Q'

The net heat given to the high-temperature reservoir is $|Q| = |Q_H'| - |Q_H|$

from Eq I, we have

$$|Q| = |Q_H'| - |Q_H| = |Q_L'| - |Q_L|$$

Therefore the net heat extracted from the low-temperature reservoir is equal to the net heat discharged to the high-temperature reservoir. It means that the combination of two engines is equivalent to a perfect refrigerator by which $|Q|$ heat is transferred from low-temperature to high temperature reservoir with* any external work done. which is the violation of second law of thermodynamics. Therefore the violation of Carnot theorem is also the violation of second law of thermodynamics.

without

The Carnot's work was complete long before Clausius and Kelvin, but the Carnot theorem is a necessary consequence of the second law of thermodynamics. Hence the efficiency of any heat-engine (irreversible) ~~Carnot the~~ is always less than the efficiency of Carnot engine (reversible),

or

$$e_X < e \quad \text{and} \quad |Q_H'| < |Q_H|$$

The summary of Carnot's Theorem is

$$e = e_{carnot} \quad (\text{reversible})$$

$$e < e_{carnot} \quad (\text{irreversible})$$

Triple Point

The temperature at which ice, liquid water, and water vapour coexist in equilibrium, which is also very close to the normal freezing point of water, is called the triple point of water.

$$T_{tr} = 273.16\ K = 0.16\ ^\circ C$$

Q. Prove that the thermodynamic temperature scale (Kelvin Scale) is identical to ideal gas temperature scale.

THERMODYNAMIC TEMPERATURE SCALE AND IDEAL GAS TEMPERATURE SCALE

The efficiency of carnot engine (reversible or ideal engine) is independent of the working substance and depends only on two temperatures or (heat energies) between which the engine operates. Therefore the efficiency is given by

$$e = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|} \quad \text{---- I}$$

Let θ_L and θ_H are the temperatures on thermodynamic scale (Kelvin scale), between which the engine operates. Here $|Q_H|$ is the heat absorbed by the engine from a high temperature reservoir at temperature 'θ_H' and 'Q_L' is the heat rejected by the engine to low-temperature reservoir at temperature θ_L

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Therefore the efficiency
is also given by

$$e = \frac{\theta_H - \theta_L}{\theta_H} = 1 - \frac{\theta_L}{\theta_H} \quad \text{------} \ \mathrm{II}$$

From Eq I and Eq II, we have.

$$\frac{\theta_L}{\theta_H} = \frac{|Q_L|}{|Q_H|} \quad \text{----}$$

If θ_{tr} is the triple point of water, then

$$\theta_{tr} = 273.16\ K. \quad {}^\circ C = 0$$

Let the carnot engine is operating between the temperatures 'θ' and 'θ_{tr}' for which the corresponding heat energies are $|Q|$ and $|Q_{tr}|$
Then we have

$$\frac{\theta}{\theta_{tr}} = \frac{|Q|}{|Q_{tr}|} \qquad \boxed{\theta = 273.16K \frac{|Q|}{|Q_{tr}|}} \quad \text{----} \ \mathrm{III}$$

Let 'T' and 'T_{tr}' are the temperatures on ideal gas scale, Then we have

$$\frac{T}{T_{tr}} = \frac{X}{X_{tr}}$$

(Here 'X' is the thermometric property of the system

as Set $T_{tr} = 273.16\ K$ (triple point of water)

Therefore

$$\boxed{T = 273.16\ K\ \frac{X}{X_{tr}}} \quad \text{---} \ \mathrm{IV}$$

In Eq III $|Q|$ acts like thermometric property.
Therefore the efficiency of the carnot engine

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P ; Notes for 11 LCCCLHR

As $\frac{|Q|}{|Q_{tr}|} = \frac{X}{|X_{tr}|} = \frac{T}{T_{tr}}$

Therefore

$$e = \frac{|Q_H| - |Q_L|}{|Q_H|} = \frac{\theta_H - \theta_L}{\theta_H} = 1 - \frac{\theta_L}{\theta_H} \quad \ldots \text{V}$$

Also

$$e = \frac{|Q_H| - |Q_L|}{|Q_H|} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H} \quad \ldots \text{VI}$$

Comparing Eq V and Eq VI, we get.

$$\frac{\theta_L}{\theta_H} = \frac{T_L}{T_H}$$

Similarly

$$\frac{\theta}{\theta_{tr}} = \frac{T}{T_{tr}}$$

The triple point is $\theta_{tr} = T_{tr} = 273.16$ K

therefore

$$\theta = T$$

Hence the temperature on Thermodynamic scale (Kelvin scale) is identical to the temperature on ideal gas scale.

__Zeroth law of thermodynamics__ This law may be stated as

"If systems A and B are each in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other"

It means that, if the temperature of system 'A' is equal to that of system C, similarly the temperature of system B is also equal to that of system C. Then the temperature of A is equal to the temperature of system B.

Discuss entropy and reversible cycle.

ENTROPY AND REVERSIBLE CYCLE

Considering carnot cycle (which is reversible cycle) in which 'Q_H' heat is absorbed by carnot engine at constant temperature T_H and 'Q_L' is the rejected by it at constant temperature T_L.

Also, we have

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}$$

or

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

As 'Q_L' heat is rejected by the system, therefore

$$\frac{Q_H}{T_H} = -\frac{Q_L}{T_L}$$

or

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \quad \text{---- I}$$

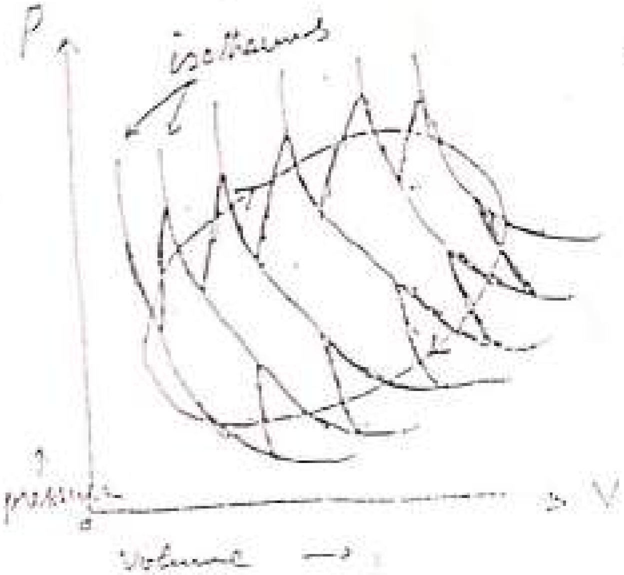
The algebric sum of the quantities $\frac{Q}{T}$ for reversible carnot cycle is equal to zero. [Claussius theorem]

To generalize Eq I, a large reversible cycle (not carnot cycle) is considered which is superimposed on a family of isothermals. These isotherms are also connected by adiabatic lines, forming an assembly of carnot cycles, is shown in the Fig.

Whole Reversible cycle

The whole reversible cycle is divided into a large number of carnot cycles.

Therefore for all these carnot cycles the algebraic sum of quantities $\frac{Q}{T}$ must be equal to zero.



or

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

In the limit of infinitesimal temperature difference between the isotherms, we have

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

This integral is for the complete reversible cycle. Here 'dQ' is a very small quantity of heat which enters or leaves the system at constant temperature T, during isothermal process.

Let $$dS = \frac{dQ}{T} \quad \text{----} \; II$$

Therefore $$\oint dS = 0 \quad \text{---} \; III$$

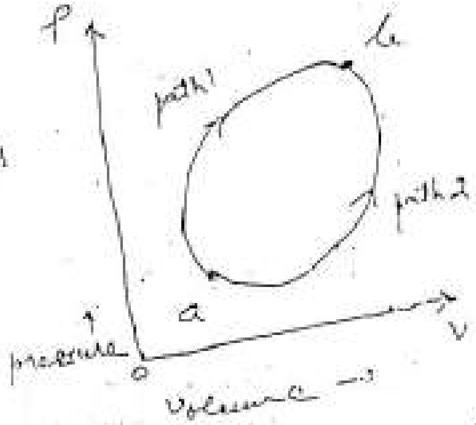
Here 'S' is the entropy of the system and 'dS' is the very small change in the entropy of the system. The Eq. III states that

...l change in ...py of the system ...ing a reversible cycle is equal to zero."

- The unit of entropy is J/K.

The mathematical form of second law of thermodynamics is

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



Consider a reversible cycle which consists of two paths between any two points a and b, as shown in the Fig.

In a reversible cycle the total change in entropy is equal to zero, therefore

$$\oint dS = 0$$

$$\Rightarrow \int_{a\ (\text{path 1})}^{b} dS + \int_{b\ (\text{path 2})}^{a} dS = 0$$

$$\Rightarrow \int_{a\ (\text{path 1})}^{b} dS - \int_{a\ (\text{path 2})}^{b} dS = 0$$

$$\Rightarrow \int_{a\ (\text{path 1})}^{b} dS = \int_{a\ (\text{path 2})}^{b} dS$$

CA (21) P (57)

It means the value of the integral (between two equilibrium states)

$\int_a^b dS$ is independent of the path followed

Therefore 'dS' is an exact differential.

The change in entropy of the system between any two states i & f is

$$\int_i^f dS = \int_i^f \frac{dQ}{T}$$

$$\boxed{\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}}$$

This integral is evaluated over any reversible path connecting the states i and f.

Therefore entropy 'S' is also a state variable like the other state variables, like temperature T, volume V, pressure P and internal energy E_{int}. These variables a combination determine the ~~state of~~ a system

Q. Discuss the change in entropy during irreversible processes.

ENTROPY AND IRREVERSIBLE PROCESSES

A reversible process is an ideal process but a real process is an irreversible process due to friction and unwanted heat transfers. Therefore there is an irreversible path between two states i & f for the actual process or real process.

To find the entropy change for an irreversible path between two equilibrium states, find a reversible process connecting the same states and calculate the entropy change using equation

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

~~Hence~~

FREE EXPANSION: Free expansion is an example of irreversible process, because we lose control of the system once we open the valve that separates the two cylinders of the gas. Therefore the entropy of the system changes between initial and final states. There is an irreversible path between initial state i and the the final state f, and the intermediate states are nonequilibrium. But the change in entropy cannot be determined by following the irreversible path. Therefore a reversible path is considered which is the isothermal process between two equilibrium states, state i (P_i, V_i, T) and state f (P_f, V_f, T) which are also the initial and final states of irreversible path.

Isothermal Process