UNIT-II

ENTROPY:

Entropy - change in entropy in reversible and irreversible processes - temperature - entropy diagram - Clausius - Clayperon equation - Enthalpy - Nernst heat theorem.

Thermal conductivity - forbe's method, Lee's disc method - Thermal conductivity of glass and rubber.

What is entropy?

The word entropy is sometimes confused with energy. Although they are related quantities, they are distinct.

Or energy measures the capability of an object or system to do work.

On the other hand, is a measure of the "disorder" of a system. What "disorder refers to is really the no. of different microscopic states a system can be in, given that the system has a particular fixed composition, Volume, energy, pressure, and temperature. By "microscopic states" we mean the exact states of all the molecules making up the system.

Entropy = (Boltzmann's constant k) × logrithm of no. of possible states
$= k \log(N)$.

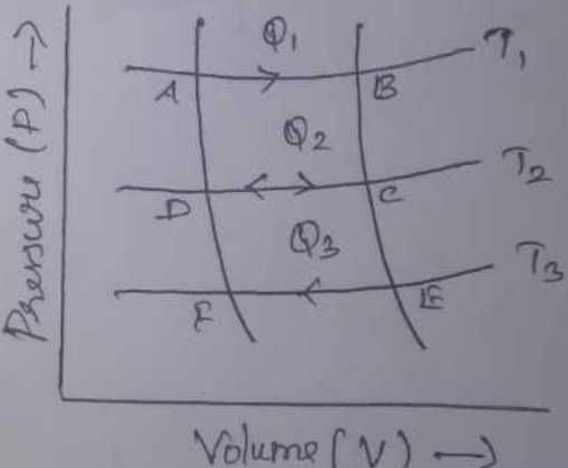
Entropy:

Definition: The entropy of a substance is that physical quantity which remains constant when the substance undergoes a reversible adiabatic process.

Explanation:

Consider two adiabatics AF and BE. Crossed by a no. of isothermal at temp T_1, T_2, T_3.

Consider the carnot cycle ABCD. Let Q_1 be the heat absorbed from A to B at temperature T_1. Let Q_2 be the heat rejected from C to D at temp. T_2.



Then, from the theory of Carnot engine, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$.

||ly, Consider the Carnot cycle DCEF. Q_2 is the heat absorbed at temp T_2 and Q_3 heat rejected at temp T_3. Then, $\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \text{constant.}$$

Thus, if Q is the amount of heat absorbed or rejected in going from one adiabatic to another along any isothermal at temp. T, the

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

This constant ratio is called the change in entropy in going from the adiabatic AF to the adiabatic BE.

If a system absorbs a quantity of heat dQ at constant temp. T during a reversible process, the entropy increases by

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

Ily, if a substance gives out a quantity of heat dQ at temp. T. during a reversible change, then its entropy decreases by

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

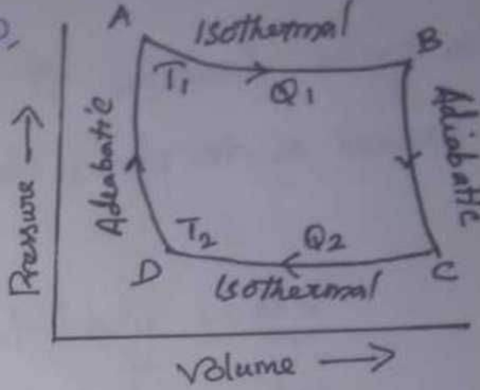
unit of entropy is JK^{-1}

For an adiabatic change we have $dQ = 0$.

$$\therefore dS = 0$$

Thus, there is no change of entropy during a reversible adiabatic process.

Change of entropy in a reversible process



Consider a reversible Carnot cycle ABCD,

(i) In the isothermal expansion from A to B, the working substance absorbs an amount of heat Q_1 at a constant temp. T_1.

$$\left.\begin{array}{c}\text{Increase in entropy of working} \\ \text{Substance from A to B}\end{array}\right\} = \frac{Q_1}{T_1}$$

(ii) During the adiabatic expansion from B to C there is no change in entropy.

(iii) During the isothermal compression from C to D, the working substance gives out a quantity of heat Q_2 at a constant temp. T_2

Decrease in entropy of working substance from C to D $= \frac{Q_2}{T_2}$

(iv) During the adiabatic compression from D to A, there is no change in entropy.

$$\therefore \left.\begin{array}{c}\text{The net change in entropy of the working} \\ \text{substance during the cycle ABCD}\end{array}\right\} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

For a reversible cycle,

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

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

Thus, the total change of entropy is zero during a Carnot's cycle. Entropy change in a reversible cycle is zero.

Change in entropy in an irreversible process:

Consider an irreversible process like conduction or radiation of heat.

Suppose a body at higher temp. T_1 conducts away a small quantity of heat dQ to another body at a lower temp. T_2 then,

decrease in entropy of the hot body $= \frac{dQ}{T_1}$

increase in entropy of the cold body $= \frac{dQ}{T_2}$

$\therefore$ The net increase in the entropy of the system $= ds = \frac{dQ}{T_2} - \frac{dQ}{T_1}$.

ds is always positive since $T_1 > T_2$. Hence there is an increase of entropy.

ll'y, there is an increase of entropy during the loss of heat by radiation.

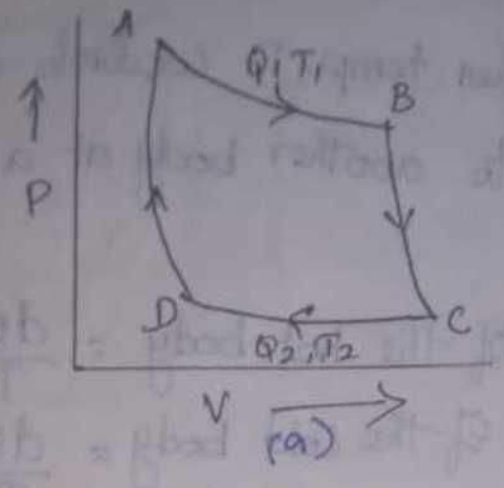
$\therefore$, generally, the entropy of a system increases in all irreversible processes. This is called the law of increase of entropy.

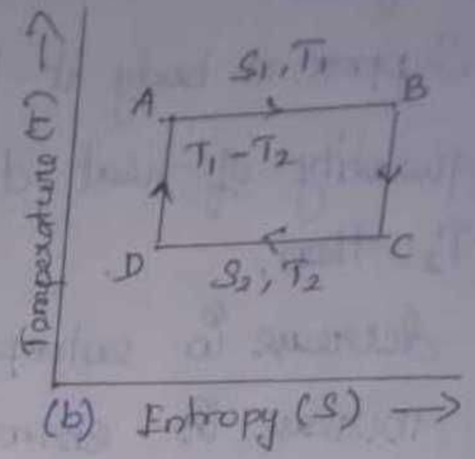
Temperature - entropy diagram:

The state of a substance may be represented by points plotted with temp. as ordinates and entropies as abscissae. This is the TS diagram.

Here the isothermals are horizontal straight lines (parallel to S-axis). The adiabatics are vertical straight lines (parallel to T-axis).

Consider the Carnot cycle. ABCD, (Fig. a)





(i) From A to B, heat energy Q_1 is absorbed at temp. T_1. The increase in entropy S_1 takes place from A to B (Fig. b)

$$S_1 = \frac{Q_1}{T_1} \quad — ①$$

(ii) From B to C there is no change in entropy. Fall of temp. is $T_1 - T_2$.

(iii) From C to D, there is decrease in entropy (S_2) at constant temp. T_2.

$$S_2 = \frac{Q_2}{T_2} \quad — ②$$

(iv) From D to A, there is no change in entropy but the temp. increases from T_2 to T_1.

The area ABCD in the T-S diagram $= S_1(T_1 - T_2) = S_2(T_1 - T_2)$

$$S_1 = S_2 = \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2} \quad — ③$$

$\therefore$ Area of figure ABCD in T-S diagram $\Big\} = \frac{Q_1 - Q_2}{T_1 - T_2}(T_1 - T_2) = Q_1 - Q_2$

— ④

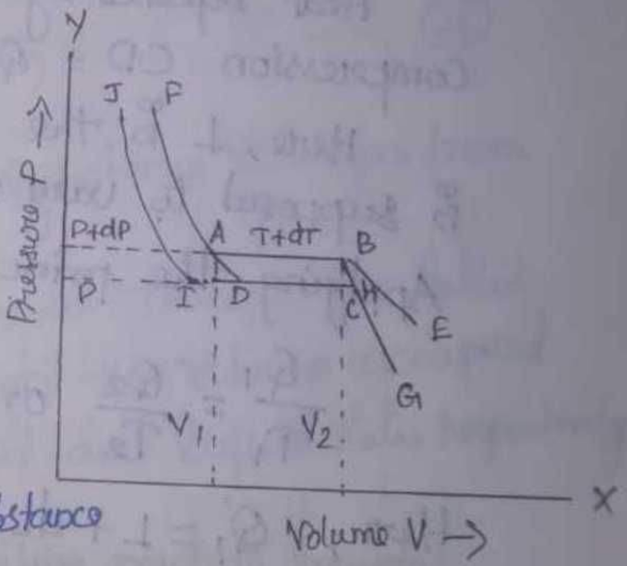
The area ABCD represents the energy converted to work.

The efficiency of the engine,

$$\eta = \frac{\text{Heat energy converted into work}}{\text{Total heat absorbed}}$$

$$\eta = \frac{S_1(T_1 - T_2)}{T_1 S_1} = \frac{T_1 - T_2}{T_1}$$

CLAUSIUS CLAPEYRON'S EQUATION



Let GHIJ and EBAF represent two isothermals of a substance at temp. T and T + dT respectively.

Let both these temps. be below the critical temperature.

=) At the point A and I, the substance is purely in the liquid state.

=) From A to B or I to H, the system is in transition from the liquid to the gaseous state.

=) At B and H, the substance is purely in the gaseous state.

=) Therefore, T is the boiling point of the liquid at pressure P and T + dT is the boiling point at pressure P + dP.

Let V_1 and V_2 be the volumes of the substance at A and B respectively. From A and B draw adiabatic to meet the lower isothermal at D and C respectively.

Suppose that 1 kg of the substance is taken round a reversible Carnot cycle ABCD allowing it to expand isothermally along AB, adiabatically along BC, compressing it isothermally along CD and adiabatically along DA.

Heat absorbed by the working substance during the isothermal expansion AB = $Q_1 = L + dL$

Here, $L + dL$ is the specific latent heat of vapourization at temperature $T + dT$.

Heat rejected by working substance during the isothermal compression CD = $Q_2 = L$.

Here, L is the latent heat at temp. T and latent heat is supposed to vary with temperature.

Applying the principle of Carnot's reversible cycle,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \text{or} \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Here, $Q_1 = L + dL$, $Q_2 = L$, $T_1 = T + dT$ and $T_2 = T$.

$$\frac{L + dL}{L} = \frac{T + dT}{T}$$

$$\text{or} \quad \frac{dL}{L} = \frac{dT}{T}$$

$$dL = \frac{L}{T} dT \qquad \text{— ①}$$

The net amount of heat converted into work during the cycle ABCD is

$$W = Q_1 - Q_2 = L + dL - L = dL \qquad \text{— ②}$$

Work done during the Carnot cycle = Area ABCD

$$= (V_2 - V_1)\,dP$$

$$\therefore \; dL = (V_2 - V_1)\,dP \qquad —— ③$$

Here, V_2 and V_1 are the specific volumes of 1 kg of the substance (m^3/kg) in vapour and liquid states respectively.

Substituting this value of dL in Eq.(1)

$$dP(V_2 - V_1) = \frac{L}{T}\,dT$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \qquad —— ④$$

Note:

This equ. is true when a substance changes from solid to liquid also.

In this case, L will represent the specific latent heat of fusion. V_1 and V_2 represent the volume occupied by 1 kg of the substance in solid and liquid states respectively.

Effect of change of pressure on boiling points of liquids:

(i) Effect of change of pressure on boiling points of liquids: When a substance changes from liquid state to vapour state, there is an increase in volume so that $V_2 > V_1$. Hence dP/dT is +ve. Thus, the boiling point of a liquid rises with increase in pressure and vice versa.

(ii) Effect of pressure on melting points of Solids:

When a solid melts, its volume may increase in some cases and decrease in some other cases.

(a) When $V_2 > V_1$ (as in wax, sulphur etc.) $\frac{dP}{dT}$ is a +ve quantity. In such cases, the melting point of the substance will increase in pressure and vice versa.

(b) When $V_2 < V_1$, (as in ice, gallium & bismuth), $\frac{dP}{dT}$ is a −ve quantity. ∴, an increase in pressure (+ve dP) cause a decrease in melting point (−ve dT)

Second Latent Heat Equation:

Let GCDH and EBAF represent two isothermals of a substance at temps T and ~~d~~ T+dT respectively.

=> Along GC and EB, the substance exists in the vapour state.

=> Along CD and BA, the change of state is in progress. The liquid and vapour states co-exist in equilibrium.

=> Along DH and AF, the substance exists in the form of liquid.

Let the specific heat capacity of the liquid be C_1.

Let the specific heat capacity of saturated vapour be C_2.

Let the specific heat of vaporization of the liquid be L at temp. T and L+dL at temp T+dT.

Suppose 1 kg of the substance is taken round the cycle ABCDA.

Along AB, the substance changes from liquid to vapour at constant temp. T+dT and it absorbs a quantity of heat L + dL. Therefore,

$$\text{increase in entropy along } AB = \frac{L+dL}{T+dT} \quad \text{—①}$$

In passing from B to C, the temp. of the substance (vapour) falls by dT. Hence it rejects a quantity of heat $C_2 dT$. We assume the temp. to be T all along BC. Therefore,

$$\text{decrease in entropy along } BC = \frac{C_2\, dT}{T} \quad \text{—②}$$

In passing from C to D, the saturated vapour condenses to liquid at constant temp. T.

Hence, it rejects a quantity of heat L. Therefore, decrease in entropy along CD $= \frac{L}{T}$ — ③

When the liquid is taken from D to A, its temp increases by dT. so that it absorbs a quantity of heat $C_1\,dT$.

∴ increase in entropy along DA $= \frac{C_1 dT}{T}$ — ④

But the total change of entropy is zero for a reversible cycle.

Hence,

$$\frac{L+dL}{T+dT} - \frac{C_2 dT}{T} - \frac{L}{T} + \frac{C_1 dT}{T} = 0$$

Multiplying throught by $T(T+dT)$,

$$T(L+dL) - (T+dT)(C_2 dT) - (T+dT)L + (T+dT)C_1 dT = 0$$

Expanding and neglecting $(dT)^2$ as too small,

$$T\,dL - C_2 T\,dT - L\,dT + C_1 T\,dT = 0$$

Dividing by $T\,dT$ throughout,

$$\frac{dL}{dT} - C_2 - \frac{L}{T} + C_1 = 0$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$ — ⑤

This is the second latent heat equation.

Thermal Conductivity:

The ability of a substance to conduct heat energy is measured by thermal conductivity.

Thermal Conduction:

It is a well known fact that heat is conducted through the materials of a body.

In conduction, heat transfer takes place from one point to another through a materials medium without the actual movement of the particles in that medium.

The heat is transmitted from a body of higher temp. to that of lower temp.

As an example, when a metal rod is heated at one end, the heat gradually flows along the length of the rod and other end of the rod also beomes hot after some time.

This shows that heat has travelled through the molecules of the rod from one end to other.

The molecules in the rod remain fixed in their mean positions.

On heating the energy of molecules increases and they start vibrating about their mean positions. They collide with the neighbouring molecules. Because of this collision, the neighbouring molecules set into vibration.

Each molecule thus transfer some of the heat it receive from its predecessor to its successor. Thus the transmission of heat takes place by molecular vibrations in the case of conduction.

Definition: It is the process of transmission of heat from one point to another through substance (or some medium) without the actual motion of the particles.

FORBE'S METHOD TO FIND K

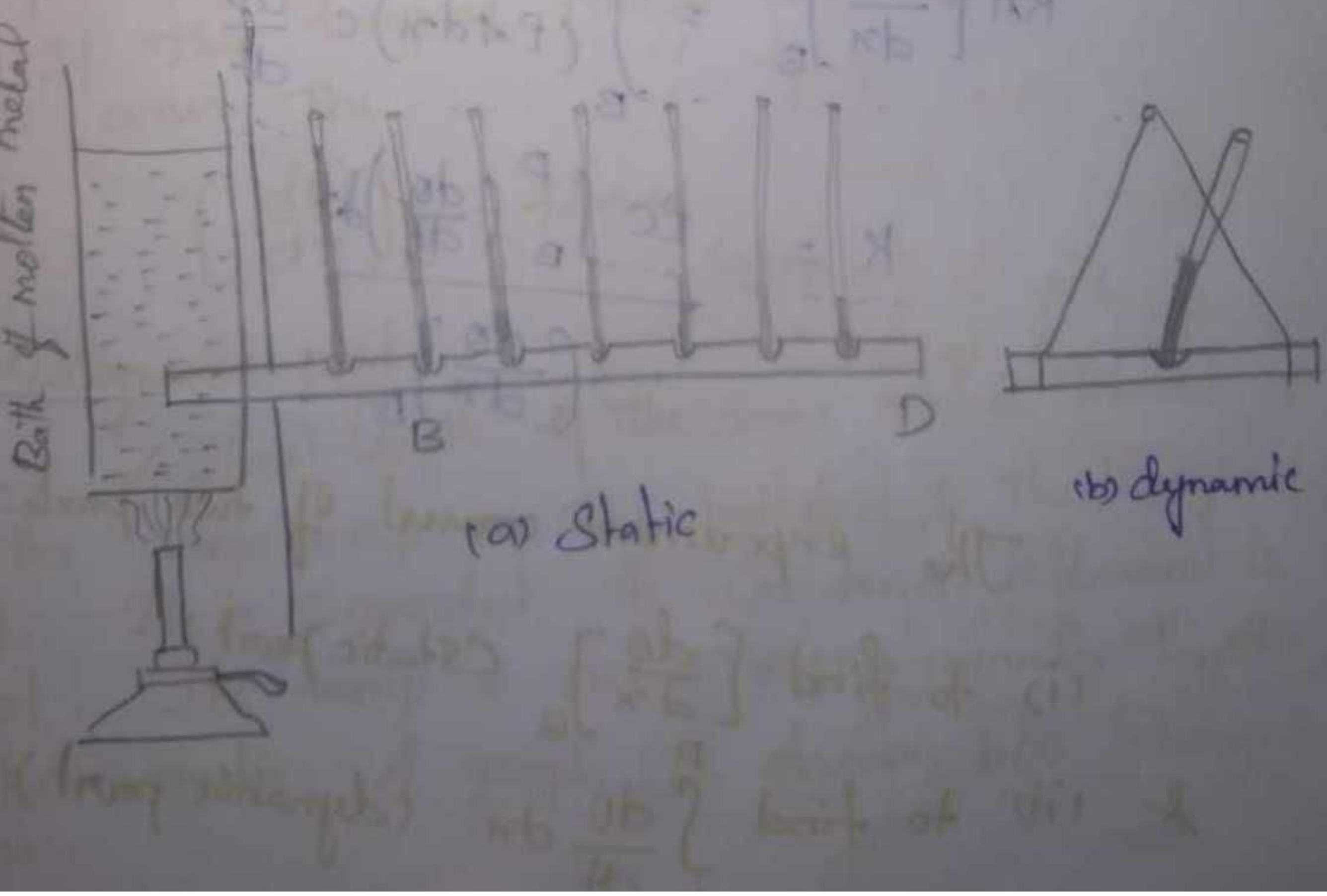
THEORY:

This method is used for the determination of the thermal conductivity of a metal.

=> Consider a metal rod of uniform cross-section heated at one end.

=> In the steady state, the amount of heat passing per second across the cross section at the point B is

$$KA\left[\frac{d\theta}{dx}\right]_B$$



(a) Static

(b) dynamic

Here, A is the area of cross-section of the rod and K is the thermal conductivity of the material of the rod.

$\left(\frac{d\theta}{dx}\right)$ is the temp. gradient at B.

The amount of heat lost by radiation per second from the point B upto the end D.

$$= \int_B^D (\rho A\, dx)\, c \frac{d\theta}{dt}$$

Here c is the specific heat capacity of the material of the rod and ρ is the density.

$$KA\left[\frac{d\theta}{dx}\right]_B = \int_B^D (\rho A\, dx)\, c\, \frac{d\theta}{dt}$$

$$K = \frac{\rho c \int_B^D \left(\frac{d\theta}{dt}\right) dx}{\left[\frac{d\theta}{dx}\right]_B}.$$

The experiment consist of two parts:

(i) to find $\left[\frac{d\theta}{dx}\right]_B$ (static part)

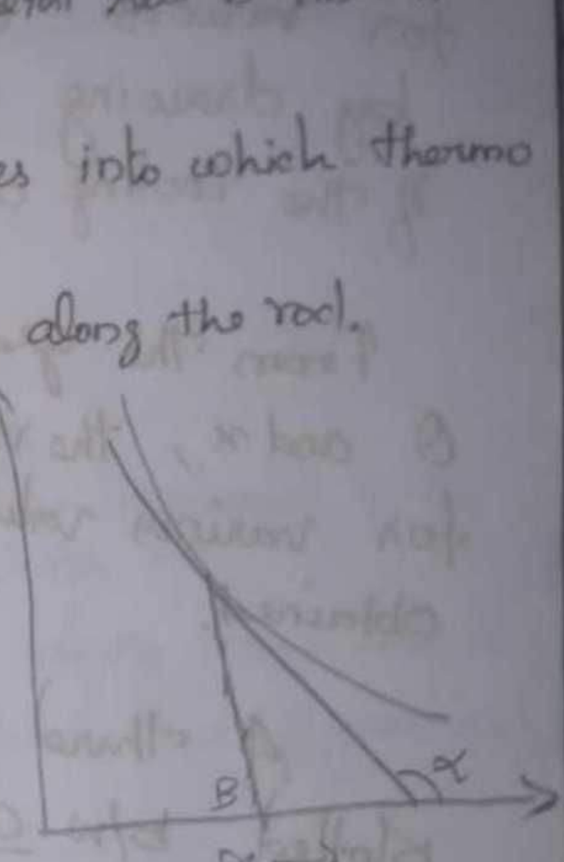
& (ii) to find $\int_B^D \frac{d\theta}{dt}\, dx$ (dynamic part).

(i) Static Part:

One end of a long uniform metal rod is immersed in molten lead.

The rod has a series of holes into which thermometers are fitted.

These temps. at different points along the rod.



When the steady state is reached, the temp θ shown by the thermometers and their distances (x) from the hot end are noted.

A graph is plotted between θ and x.

Draw a tangent to the curve at a point B.

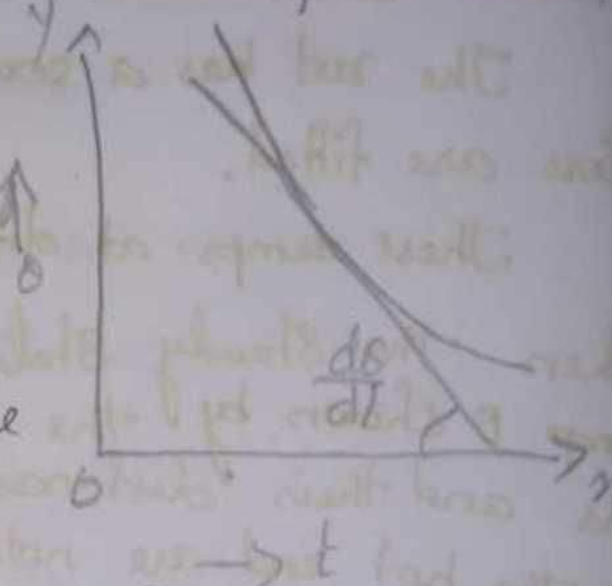
If this tangent makes an angle α with the x-axis, The

$$\left[\frac{d\theta}{dx}\right]_B = \tan\alpha$$

(ii) Dynamic part:

A short length of the same rod is heated to the same temp. as the hot end of the original rod. It is suspended in air and allowed to cool. Its temp is noted every minute by the thermometers. A graph is drawn b/w temp & time.

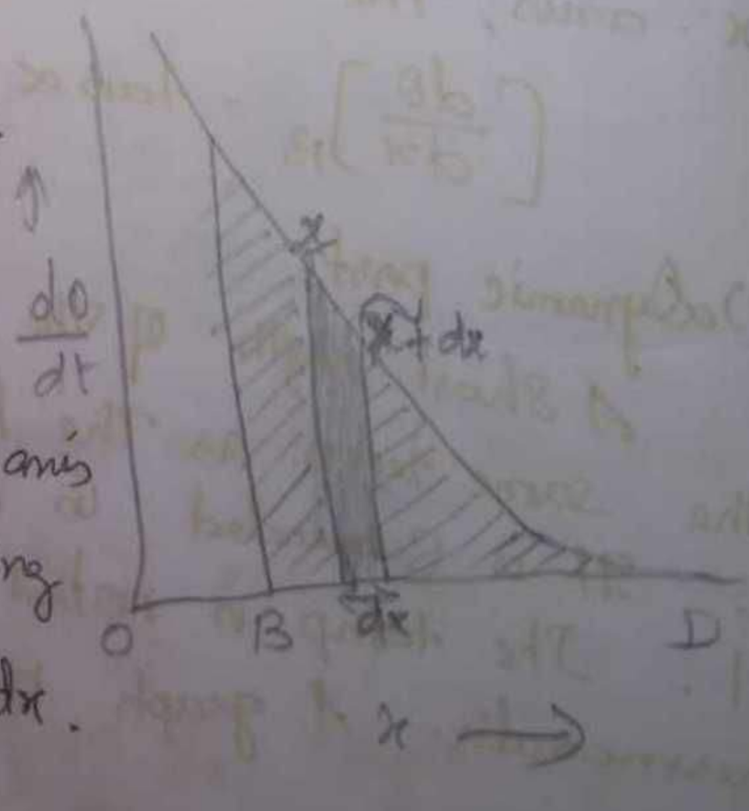
From this graph, the value of $\frac{d\theta}{dt}$ for various values of θ is determined by drawing tangents at various points of the cooling curve.



From The graph between θ and x, the value of x for various values of θ are obtained.

A third graph is now plotted b/w $\frac{d\theta}{dt}$ and the corresponding values of x.

The graph is produced to meet the x-axis corresponding to the point B, a point located on the graph.



The area bounded by the curve, the x axis and the ordinate passing through B is $\int_B^D \frac{d\theta}{dt} dx$.

The area of the shaded portion is determined.

$$\therefore K = \frac{\rho C(\text{area of the shaded portion})}{\tan \alpha}$$

Thus K is determined.

Drawbacks of the experiment:

(1) The specific heat capacity of the material of the rod does not remain constant.

(2) The ~~std~~ temp distribution along the rod is not the same in the statical and dynamical experiments.

LEE'S DISC METHOD FOR BAD CONDUCTORS:

The thermal conductivity of a bad conductors like ebonite or card board is determined by this method.

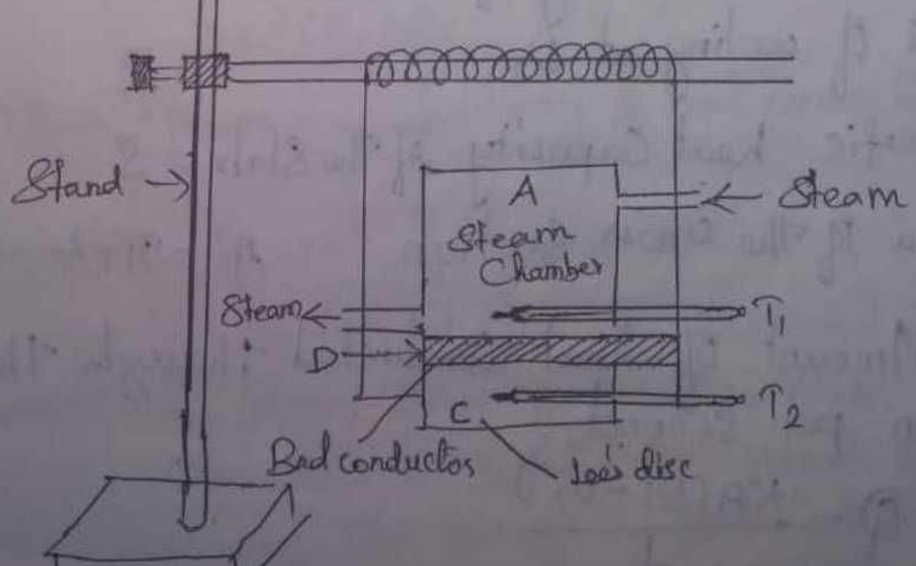
Description

The apparatus consists of a circular metal disc or slab C (Lee's disc) suspended by strings from a stand.

The given bad conductor (such as glass, ebonite) is taken in the form of a disc (D). This disc has the same diameter as that of the slab and is placed over it.

The cylindrical hollow steam chamber (A) having the same diameter as that of the slab is placed over the bad conductor.

There are holes in the steam chamber and the slab through which thermometers T_1 and T_2 are inserted to record the respective temperatures.



Working:

Steam is passed through the steam chamber until the temperature of the chamber and the slab are steady.

When the thermometers show steady temps. their readings θ_1 and θ_2 are noted.

The radius (r) of the disc D and its thickness(d) are also noted.

Observation and calculation:

Thickness of the bad conductor	= d metre
Radius of the bad conductor	= r metre
Mass of the slab (C)	= M kg
Steady temp. in the slab	= θ_1
Steady temp. in the steam chamber	= θ_2
Thermal conductivity of the bad conductor	= K
Rate of cooling at θ_2	= R
Specific heat capacity of the slab	= S
Area of the cross section	$A = \pi r^2$

Amount of heat conducted through the specimen per second

$$Q = \frac{KA(\theta_1 - \theta_2)}{d}$$

$$= \frac{K(\pi r^2)(\theta_1 - \theta_2)}{d} \quad -①$$

At this stage all the heat conducted through the bad conductor is completely radiated by the bottom flat surface and the curved surface of the slab C.

Amount of heat lost per second by the slab C.

Q = Mass × Specific heat capacity × Rate of cooling.

$$Q = MSR \quad -②$$

At steady rate,

$$\left\{ \begin{matrix} \text{Heat conducted through} \\ \text{bad conductor per second} \end{matrix} \right\} = \left\{ \begin{matrix} \text{Heat lost per second} \\ \text{by the slab C} \end{matrix} \right\}$$

Hence, the equ ① and ② are equal

$$\frac{K\pi r^2(\theta_1 - \theta_2)}{d} = MSR$$

$$\therefore K = \frac{MSRd}{\pi r^2(\theta_1 - \theta_2} \quad Wm^{-1}K^{-1}$$

Thus, thermal conductivity of bad conductor is determined.

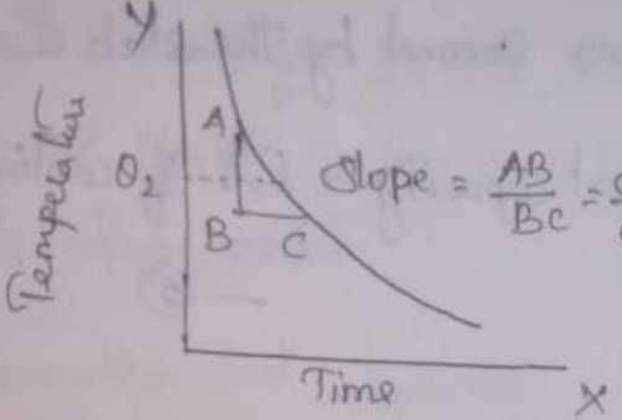
Determination of rate of cooling R:

The bad conductor is removed and the steam chamber is placed directly on the slab.

The slab is heated to a temp. of about 5°C higher than θ_2. The steam chamber is removed and the slab alone is allowed to cool.

As the slab cools, the temps of the slab are noted at regular intervals of half a minute until the temp of the slab falls to about 5° below θ_2.

The time-temp. graph is drawn. and the rate of cooling $\frac{d\theta}{dt}$ at the steady temp. θ_2 is determined



During the first part of the experiment, the top surface of the slab is covered by the bad conductor. Radiation is taking place only from the bottom surface area and curved surface area.

i.e., total area of $= \pi r^2 + 2\pi r h = \pi r(r+2h)$

Where h is the height of C.

In the second part of the experiment, heat is radiated from the top surface area, the bottom surface area and the curved sides, i.e., over an area.

$$2\pi r^2 + 2\pi r h = 2\pi r(r+h)$$

As the rate of cooling is directly proportional to the surfaces are exposed (other condition being equal)

$$\frac{R}{\frac{d\theta}{dt}} = \frac{\pi r(r+2h)}{2\pi r(r+h)} = \frac{r+2h}{2(r+h)}$$

$$R = \frac{d\theta}{dt} \frac{r+2h}{2(r+h)} \quad — \text{④}$$

Substituting this value in eqn ③,

$$K = \frac{Ms\frac{d\theta}{dt}d}{\pi r^2(\theta_1-\theta_2} \times \frac{(r+2h)}{(r+h)} \quad —\text{⑤}$$

from which K is determined.

Determination of thermal conductivity of rubber:

Experiment:

⇒ A known length of a rubber tube is kept immersed in a calorimeter (C) containing a known mass of water.

⇒ The initial temp (θ_1) of the calorimeter and contents is noted with a sensitive thermometer (T).

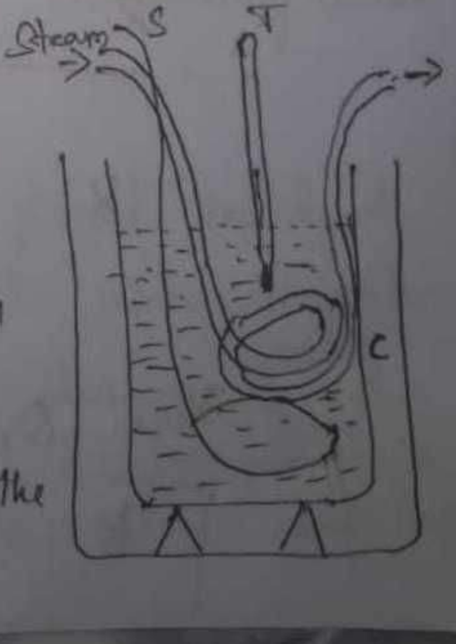
⇒ Steam is then passed through one end of the rubber tube and let off through the other.

⇒ The inner side of the tube attains the temp. of steam.

⇒ Heat flows through the wall of the tube to the outer surface in contact with the water in the calorimeter.

⇒ Steam is cut off when the temp of water rises by about 10°C.

⇒ The final corrected temp. θ_2 is noted



⇒ The time (t) for which steam is passed is noted.

⇒ The internal and external radii r_1 and r_2 of the rubber tube are measured by a microscope.

⇒ length (l) of the rubber tube inside the water is also measured.

Calculation:

Heat gained per second by the water and the calorimeter,

$$Q = (m_1 c_1 + m_2 c_2)(\theta_2 - \theta_1)/t$$

Here m_1 = mass of the calorimeter
c_1 = Specific heat capacity of the material of the calorimeter,
m_2 = mass of water.
c_2 = Specific heat capacity of water.

coefficient of thermal conductivity of rubber is then calculated using the formula

$$\to \quad K = \frac{Q \log_e\left[\frac{r_2}{r_1}\right]}{2\pi l\left[\theta_3 - \frac{(\theta_1+\theta_2)}{2}\right]}$$

$\theta_3 \to$ temp. of steam,

$\frac{\theta_1+\theta_2}{2} \to$ average temp of the water and calorimeter.

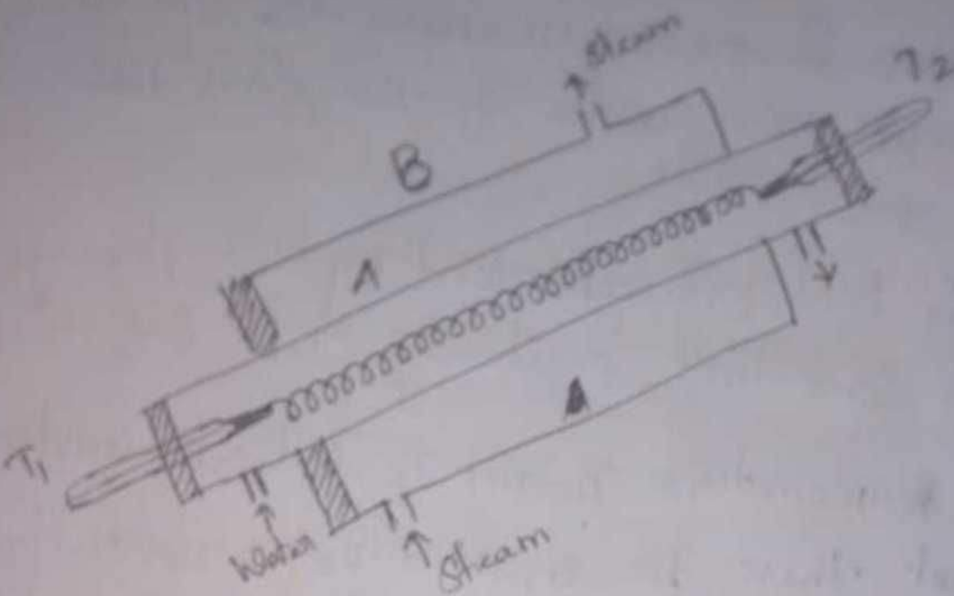
. . . ______ . x ______

$$K = \frac{Q \log_e\left[\frac{r_2}{r_1}\right]}{2\pi l(\theta_1 - \theta_2)} \; W\text{-}m^{-1}\text{-}K^{-1}.$$

Here $\theta_1 = \theta_3$, $\theta_2 = \frac{\theta_1+\theta_2}{2}$

$$\boxed{K = \frac{Q \log\left[\frac{r_2}{r_1}\right]}{2\pi l\left[\theta_3 - \frac{\theta_1+\theta_2}{\theta_2}\right]}}$$

Thermal conductivity of Glass:



Experiment:

=> A glass tube A is enclosed in a bigger tube C through which steam can be passed.

=> Water from a constant-head supply is passed through A at a steady rate.

=> The thermometers T_1 and T_2 measure the temp. of the inflowing and outflowing water respectively.

=> A spiral wire is placed inside A along its length in order that the water may be in good contact with the inner surface of A.

=> The whole apparatus is arranged in a slanting position, so that the flow of water is from a lower to a higher level. This also helps for good contact of water with the inner walls of the tube A

As steam is passed through the Jacket C, heat flows through the walls of the glass tube towards its axis.

This heat is absorbed by the flowing water. After some time a steady state is reached

The thermometers T_1 and T_2 indicate constant readings. Let these be θ_1 and θ_2 respectively.

The out-going water is now collected in a weighed beaker, for a known time t. It mass m is determined. The length (l) of the tube A exposed to steam is measured.

The internal and external radii r_1 and r_2 of the tube are measured by a travelling microscope.

Calculation: The conductivity k of the glass is calculated using the formula.

$$K = \frac{Q \log_e \left[\frac{r_2}{r_1}\right]}{2\pi l \left[\theta_3 - \left[\frac{\theta_1 + \theta_2}{2}\right]\right]}$$

Here, θ_3 = temp of steam,

$(\theta_1 + \theta_2)/2$ = average temp of water flowing through the tube

Q - Quantity of heat flowing through the tube.