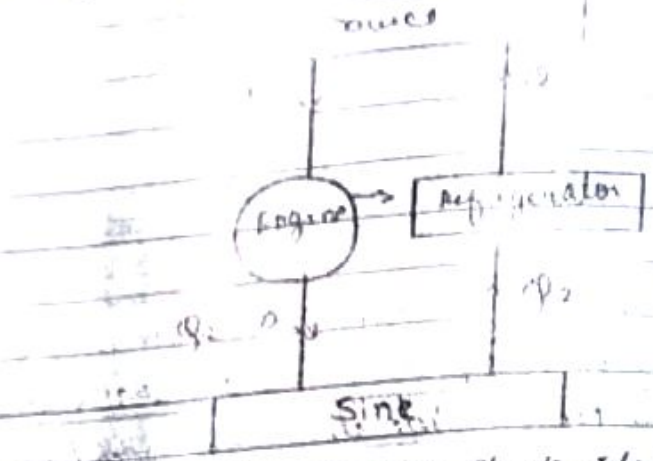
Let think of an engine which extracts an amount of heat Q_1 from hot body and converse all heat without rejecting any to the cold body



Thus it violets the Kelvin Plank statement Now suppose that a refrigerator also work in betⁿ the same two cold body. It extracts an amount of heat Q_2 from cold body.

Let an amount of work $[W = Q_1]$ be done upon it so that it finally delivers an amount of heat $Q_1 + Q_2$

If the engine and refrigerator are coupled together & work simultaneously they will constitute a self acting machine extracting a heat Q_2 from cold body and delivering it to the hot body. Such a system will the clausis statement of 2nd law

Carnot's theorem

This theorem consists of two

1) No engine working b/w two given temp can be more efficient than a reversible (carnot) engine working b/w the same limits of temp (i.e b/w the source and sink).

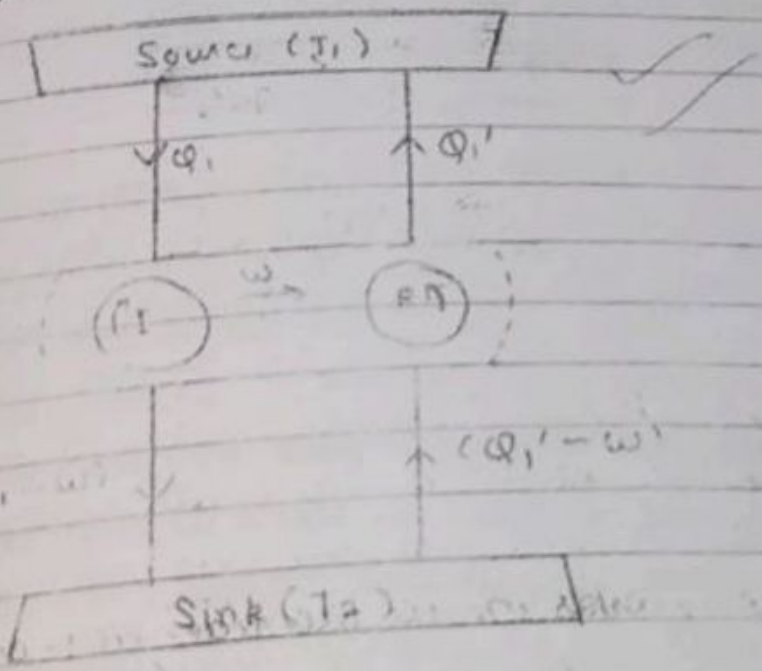
2) All reversible engines working b/w the same limits of temp have the same efficiency whatever be the working substance.

Or,

working b/w two given temp T_1 of hot (source) reservoir and T_2 of cold reservoir (sink), no efficiency more than carnot engine.

3) The efficiency of the carnot engine working b/w the same limits of temp have the its independent of nature of the working substance.

Proof :-



Let's consider (I) irreversible engine and working b/w the same sink and source.

Let engine I absorbs an amount of heat Q_1 from the source, perform an external work (W) and

reject a quantity of heat $(\varphi_1 - \omega)$ to sink.

Therefore efficiency of engine (I):-

$$\eta_I = \frac{\omega}{\varphi_1}$$

Since the similarly if the engine R, absorbs the heat from the source, does an external work (ω) and $(\varphi_1' - \omega)$ heat to the sink, then its efficiency

$$\eta_R = \frac{\omega}{\varphi_1'}$$

Suppose that engine I is more efficient than R i.e, $\eta_I > \eta_R$

$$\Rightarrow \frac{\omega_1}{\varphi_1} > \frac{\omega}{\varphi_1'}$$

$$\Rightarrow \varphi_1' > \varphi_1$$

Thus $(\varphi_1' - \varphi_1)$ is a +ve quantity

Now suppose that the two engines I & R are coupled together by a belt in such a way that engine (I) directly and it drives engine (R) backward. Engine now works as a refrigerator driven by I. Extract $(\varphi_1' - \omega)$ from sink, require (works) (ω) to be done it as given φ_1' heat to the source.

In this way, the engine I and the refrigerator coupled together form a self acting machine.

The source now looses Q_1 heat to I and gains Q_1' from R therefore heat gained by source $= [Q_1' - Q_1]$
The sink gained $[Q_1 - W]$ heat from I and gives $(Q_1' - W)$ to R therefore heat lost by sink $= (Q_1 - W) - (Q_1' - W)$
$= Q_1' - Q_1$

Thus the coupled device is transfering an each cycle an amount of heat $(Q_1' - Q_1)$ from the sink at lower temp to the source at higher temp without any add of external energy (violation of clausis law) the transformation without any expenditure of work is contrary to the II law of thermodynamics and hence it is impossible to follow; therefore our original assumpt that the irreversible engine is more efficient than the reversibe is wrong = Hence no engine can be more efficient than the reversible engine working b/w the same temp.

:-

In order to prove the 2nd part of theorem :-
Let us imagine the reversible engine (R) instead of irreversible engine R & R' working b/w the same Sour & sink. Proceeding exactly as above we can show that if we assume R to be more efficient than R', it would leadt a result which would violet the 2nd law of thermodynamics

Hence R cannot be more efficient than R'. Similarly if we assume that R' is more efficient than R, same result follows hence R' can't be more efficient than R.

ie R & R' both are of same efficiency and it is independent of nature and property of substance.

Kelvin's absolute or thermodynamical scale of temp

The efficiency of a reversible carnot engine working only upon two temp b/w which it works is independent of the property of working substance it is a property which absolutly depends on temp

Using these return worked out the theory of the Scale of temp.

Suppose a reversible engine takes in a quantity of heat at θ_1 and rejects a quantity of heat ϕ_2 at θ_2 temp the efficiency of engine is a function of these two

$$\text{Therefore } \eta = 1 - \frac{\phi_2}{\phi_1} = f(\theta_1, \theta_2)$$

$$\frac{\phi_1}{\phi_3} = \frac{1}{1 - f(\theta_1, \theta_2)} = f(\theta_1, \theta_2) \quad -(1)$$

where f is some other function of θ_1 & θ_2 similarly reversible engine works b/w a pair of temp θ_2 & θ_3 a heat ϕ_2 and rejecting the heat ϕ_3

$$\frac{\phi_2}{\phi_3} = f(\theta_2, \theta_3) \quad -(2)$$

If the engine works b/w the temp θ_1 & θ_3

$$\frac{\phi_1}{\phi_3} = f(\theta_1, \theta_3) \quad -(3)$$

Dividing eqn (2) & (1) multiplying.

$$\frac{\phi_1}{\phi_2} \times \frac{\phi_2}{\phi_3} = f(\theta_2, \theta_3) \times f(\theta_1, \theta_2)$$

$$\frac{\phi_1}{\phi_3} = f(\theta_2, \theta_3) \times f(\theta_1, \theta_2)$$

comparing with eqn (1) $\Rightarrow f(\theta_1, \theta_3) = f(\theta_1, \theta_2) f(\theta_2, \theta_3)$ — (4)

Eqn (4) doesn't contain θ_2 on left hand side therefore function f should be chosen so that θ_2 disappear from right side also.

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

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

where ϕ is another temp cons therefore from eqn (4)

$$f(\theta_1, \theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \times \frac{\phi(\theta_2)}{\phi(\theta_3)}$$

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

Now eqn (1) can be written as

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

Since $\theta_1 > \theta_2$ and $Q_1 > Q_2$

the function $\phi(\theta_1) > \phi(\theta_2)$

Thus function $\phi(\theta)$ as linear function of θ can be used to measure temp.

Suppose that $\phi(\theta)$ represent a temp. τ (some multipl. of θ) on a new scale.

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2} \quad \text{— (5)}$$

This eqn (5) define,

The Kelvin or absolute or thermodynamical temp. scale

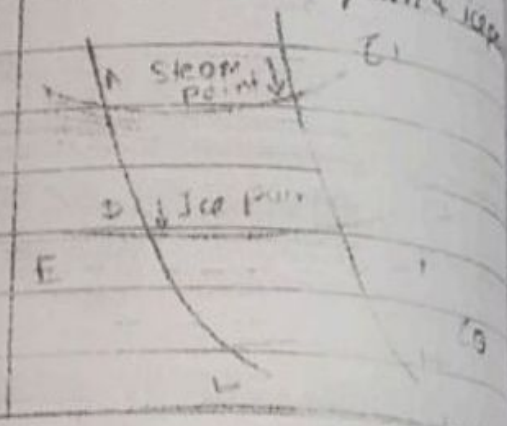
The ratio of two temp on these scale is equal to ratio of heat absorb or rejected by Carnot engine (reversib working b/w these two temp.

• The size of a degree and zero on absolute temp

The efficiency of a reversible engine can be writt

$$\eta = 1 - \frac{Q_2}{Q_1} \rightarrow 1 - \frac{T_2}{T_1} \quad \text{--- (1)}$$

Let us now considered a reversible engine working b steam point and ice point. Let ABCD represent the indicator diagram of Carnot cycle for the operat where AB & CD are isothermal for steam point & ice



$$\eta = 1 - \frac{T_{ice}}{T_{steam}}$$

$$\eta = \frac{T_{steam} - T_{ice}}{T_{steam}}$$

The work done by the engine is numerically given by ABCD. Let these area be divided into 100 equal parts drawing isothermal parallel to AB & CD.

Every isothermal will be at temp 1° lower than isother just above it and the area of each part will correspond 1° on the absolute scale. Thus the diff^n in temp b/w steam and ice point is 100 on this scale also.

Now if we draw isothermal below the ice point an isot representing the zero of this scale can be obtain & the isothermal LM represent the zero known as absolute ze

Suppose an engine working b/w steam point and absolute zero ($T_2 = 0$) then efficiency of such an engine is given by

$$\eta = 1 - \frac{T_0}{T_{steam}} = 1 \Rightarrow \boxed{\eta = 1}$$

i.e the engine has an efficiency equal to unity if we consider an engine working b/w ice point and absolute zero ($T_0 = 0$) then its efficiency will be

$$\eta = \frac{T_0}{T_{0\,ice}} = 1$$

$$\boxed{\eta = 1}$$

i.e the engine has an efficiency equal to unity But efficiency of an engine is given by

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

$$1 - \frac{Q_2}{Q_1} = 1 \quad , \frac{Q_2}{Q_1} = 0$$

$$\boxed{Q_2 = 0}$$

Thus the zero of absolute scale is that temp. of sink at which no heat is rejected to it and efficiency of engine is unity i.e

i.e the all heat taken by engine through source is converted into work.

Negative temperature is not possible

To prove it let T_2 has a negative temp. i.e $T_2 = -K$ then efficiency of engine

$$\eta = 1 - \frac{T_2}{T_1} = 1 + \frac{K}{T_1}$$

$$\boxed{\eta > 1}$$

i.e efficiency of engine is greater than unity which is against laws of 2nd law of thermo

Identity of perfect gas scale & absolute scale

The efficiency of carnot engine using a perfect gas as the working substance is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad -(1)$$

where Q_1, Q_2 are amount of heat taken from the source to sink, T_1, T_2 are the corresponding temp measured on perfect gas scale.

On absolute scale the efficiency of engine is given by —

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\tau_2}{\tau_1} \quad -(2)$$

comparing (1) & (2)

$$\frac{T_2}{T_1} = \frac{\tau_2}{\tau_1} \quad -(3)$$

i.e. the ratio of any two on the absolute scale is the same as on the perfect gas scale. If in eqn (3) $T_2 = 0$, we must also have $\tau_2 = 0$, so that the 0 of absolute scale is identical with the zero of perfect gas scale.

T_{steam}, T_{ice} are steam and ice point measured on the perfect gas scale, $T_{steam} - T_{ice} = 100$ (4)

On the absolute scale, for the same two fixed point we have $\tau_{steam} - \tau_{ice} = 100$ (5)

On the perfect scale gas efficiency

$$\eta = 1 - \frac{T_{ice}}{T_{steam}} = \frac{T_{steam} - T_{ice}}{T_{steam}} = \frac{100}{T_{steam}}$$

On absolute scale the efficiency

$$\eta = 1 - \frac{\tau_{ice}}{\tau_{steam}} = \frac{\tau_{steam} - \tau_{ice}}{\tau_{steam}} = \frac{100}{\tau_{steam}}$$

Efficiency must be same in either case

η_{steam} ... η_{steam}

$\eta_{steam} = \eta_{steam}$

i.e the steam point on perfect gas scale has the same numerical value comparing eqn (1) & eqn (2), we have,

$T_{ice} = T_{ice}$

i.e the ice point is same on the two scales

Therefore in general we conclude that the temp on perfect gas scale agrees with the corresponding temp t. Thus absolute scale is completely identical with perfect gas scale.

Internal combustion Engine

In an internal combustion engine in which the heat generated inside the cylinder. These are of two types:-

1) otto engine :- otto engine in which heat is absorbe at cons. volume

2) Diesel Engine :- Diesel engine in which heat is absorbe at cons. pressure.

1) otto Engine

It consist of a cylinder fitted with the piston. the cylinder consists of a inlet value I or outlet valve O. Its opening and closing of these value are controlled by the motion of the piston. The working substance is a mixture of gas & air.

There are four strokes in a complete cycle :-

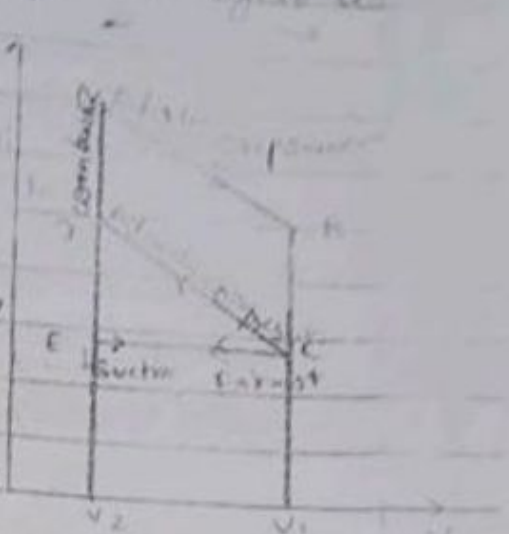
1) Suction stroke
In these stroke the initial valve I is open and a mixture of air and gas is sucked into the cylinder the forward moving piston.

2) Compression stroke
During these stroke both the initial and outlet valve closed and the mixture is compressed adiabatically to abt 1/5 of it's original volume by the backward motion of the piston as a result the temp of mixture is raised to about 600°c. At the end of these process the mixture fired by the series of spark.

3) Working Stroke
During these process both inlet and outlet valve remains closed. Due to combustion a large amount of heat is produced which raises the temp to the mixture is about 2000°c a corresponding high pressure is developed due to this the piston is thrown forward with great force
As a result the mixture expand adiabatically due to adiabatic expansion there is drop in pressure and temp of mixture. It is the stroke in which the engine performs external work.

4) Exhaust stroke
At the end of working substance stroke the cylinder is filled with a mixture of gases which is unless for further use. The outlet valve O is then open and the piston moves backward forces mixture gases out of the exhaust is complete a fresh mixture of gas (air is sucked in and the process is began.

The P-V or indicator diagram for one cycle is shown in figure



The portion BC represent the isobaric suction or charging stroke. CD represents the adiabatic compression stroke, the volume V from V1 to V2 at point D at which pressure abt 5 atmp and temp about 600°C, the mixture is ignited by the series of sparks as a result a large amount of heat is liberated this process is shown by portion DA at point A, the pressure become nearly 15 atmp and temp about 2000°C but the volume V2 remains cons. The portion AB represent the working stroke which indicates an adiabatic expansion of mixture from volume V2 to volume V1. During this process the mixture suffers drop in temp and pressure at B, at the exhaust valve is open and pressure falls to atmospheric press at C at cons volume.

CB represents the isobaric exhaust stroke. If TA, TB Tc, TD are the temp at point A, B, C, D resp & Cv the mo Specific heat at cons volume.

Then for 1gm mole of the mixture the amount of heat taken from the process DA

$$Q_1 = C_v (T_A - T_D) \quad [\because Q = mc_v dT, \; m = 1]$$

and amount of heat rejected, during the proce

BC ⇒ $Q_2 = C_v (T_B - T_C)$

Hence the thermal efficiency of engine

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \left[\frac{T_B - T_C}{T_A - T_D}\right] \quad (1)$$

Since point B & A lie on the same adiabatic

$$T_B V_1^{\gamma-1} = T_A V_2^{\gamma-1} \quad (2)$$

Similarly, C & D lie on the same adiabatic, so

$$T_C V_1^{\gamma-1} = T_D V_2^{\gamma-1} \quad (3)$$

Subtracting eqn (3) from eqn (2)

$$(T_B - T_C) V_1^{\gamma-1} = (T_A - T_D) V_2^{\gamma-1}$$

$$\frac{T_B - T_C}{T_A - T_D} = \left[\frac{V_2}{V_1}\right]^{\gamma-1} = \left[\frac{1}{\rho}\right]^{\gamma-1} \quad (4)$$

where $\rho = \frac{V_C}{V_2}$ is called adiabatic compression ratio

using (4) in eqn (1) :

$$\eta = 1 - \left[\frac{1}{\rho}\right]^{\gamma-1}$$

In actual practise ρ is kept nearly 5 so taking $\rho = 5$ and $\gamma = 1.4$ we have,

$$\eta = \left[1 - \frac{1}{5}\right]^{1.4-1} = 0.52$$

$$\boxed{\eta = 52\%}$$

The efficiency of an actual engine is less than this value

⇒ Diesel Engine.

The great superiority of diesel engine over otto engine is due to specially designed cylinder which can bear maximum pressure of 34 atmp. and also in diesel engine there is no fear of explosion, since only air is compressed.

The cylinder of diesel engine is provided with three valves namely air inlet valve, fuel supply valve, exhaust valve. The engine works on four stroke principle.

1) Suction stroke :
Air inlet value is opened and pure air at atm press is drawn into cylinder by forward motion of piston.

2) Compression stroke :
All the values are closed and the air is compressed adiabatically to abt 1/15th of its initial volume by the backward motion of piston. In this process the temp is raised to 1000°C.

3) Working Stroke :
The oil supply value is opened and oil is entered the cylinder under pressure on account of high temp., the oil is so regulated that during combustion, as piston moves forward the pressure remains cons.
In this process the burning of fuel supply is held to the air at cons pressure at certain stage when temp. has raised the max. value about ebook the supply of oil is cutoff.

4) Exhaust Stroke :
Exhaust value is opened and the useless gas mixture is forced out. Now the apparatus become ready for the new cycle.

The indicator diagram is shown in fig for diesel engine.

The portion CE represents the isobaric section Stroke.

At point C, the cylinder is full of air at V_1 ... pressure. The portion CD represents the adiabatic ... stroke. At point D the volume V_2 is $V_1/2$ of that of ... The portion DA represent the isobaric burning of ... A the volume becomes V_3 and the temp about 2000° ... point A, the supply of fuel is cut off and the remaining of working stroke is represented by adiabatic expansion.

At B, the exhaust valve is oped so that the pressure ... C, the atm pressure during the process BC heat is ... to outside. The portion CE represent the exhaust ... in which useless gas mixture is forced out. Let T_A, T_B ... be it's absolute temp corresponding to A, B, C, D & C_p & C_v ... molar specific heat of air at cons pressure & volume ...

considering 1 gm mole of air amount of heat taken at cons pressure during DA

$$Q_1 = C_p(T_A - T_D)$$

and the amount of heat rejected at cons volume along ...

$$Q_2 = C_v(T_B - T_C)$$

The thermal efficiency of diesel engine is

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_v(T_B - T_C)}{C_p(T_A - T_D)} \quad \left[\frac{C_p}{C_v}\right.$$

$$\eta = 1 - \frac{1}{\gamma}\left[\frac{T_B - T_C}{T_A - T_D}\right] \quad -(1)$$

Since point A & B lie on the same adiabatic we have

$$T_B V_1^{\gamma-1} = T_A V_3^{\gamma-1}$$

$$T_B = T_A\left[\frac{V_3}{V_1}\right]^{\gamma-1} \Rightarrow T_A\left[\frac{1}{\rho_e}\right]^{\gamma-1} \quad -(2)$$

$e \rightarrow$ exp...

$\rho_e = \frac{V_1}{V_2}$ is also called adiabatic expansion ratio

Similarly point C & D lie on the same adiabatic

$T_C V_1^{\gamma-1} = T_D V_2^{\gamma-1}$

$T_C = T_D \left[\frac{V_2}{V_1}\right]^{\gamma-1}$ $\quad T_C = T_D \left[\frac{1}{\rho_c}\right]^{\gamma-1}$

Substracting eqn (3) from (1) — (3) compression

$T_B - T_C = T_A \left[\frac{1}{\rho_e}\right]^{\gamma-1} - T_D \left[\frac{1}{\rho_e}\right]^{\gamma-1}$

$\frac{T_B - T_C}{T_A - T_D} = \frac{T_D (1/\rho_e)^{\gamma-1} - T_D (1/\rho_c)^{\gamma-1}}{T_A - T_D}$ — (4)

along DA the pressure remain const $\frac{PV_1}{PV_2} = \frac{R}{R}$

$\frac{T_A}{T_D} = \frac{V_3}{V_2} = \frac{V_3}{V_1} \times \frac{V_1}{V_2} \Rightarrow \frac{1}{\rho_e} \times \rho_c$

$\frac{T_A}{T_D} = \frac{\rho_c}{\rho_e}$ $\quad \boxed{T_A = T_D \left[\frac{\rho_c}{\rho_e}\right]}$ — (5)

from eqn (4) & (5)

$\frac{T_B - T_C}{T_A - T_D} = \frac{\rho_c/\rho_e \cdot T_D (1/\rho_e)^{\gamma-1} - T_D (1/\rho_c)^{\gamma-1}}{T_D \cdot \rho_c/\rho_e - T_D}$

$= \frac{\rho_c/\rho_e \cdot (1/\rho_e)^{\gamma-1} - (1/\rho_c)^{\gamma}}{\rho_c/\rho_e - 1}$

$\frac{T_B - T_C}{T_A - T_D} = \frac{(1/\rho_e)^{\gamma} - (1/\rho_c)^{\gamma}}{1/\rho_e - 1/\rho_c}$

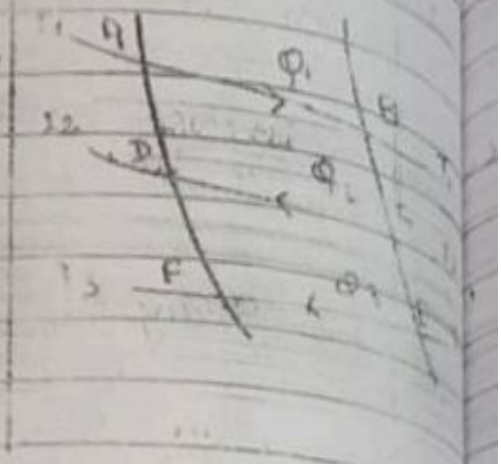
$$\boxed{\eta = 1 - \frac{1}{\gamma}\left[\frac{(1/\rho_e)^{\gamma} - (1/\rho_c)^{\gamma}}{1/\rho_e - 1/\rho_c}\right]}$$

This above eqn represents the efficiency of a diesel engine which is greater than otto engine

- Entropy

Consider a no of isothermal $I_1, I_2, I_3 \cdots$ at temp $T_1, T_2, T_3 \cdots$ on an indicator diagram.

Let A_1, A_2 be two adiabatics which intersects the isothermal at A & B, C & D, E & F.



Let ABCD & DCEF represents the carnot reversible cycle in this cycle ABCD Let Q_1 be the heat absorbed from A to B at temp T_1 and Let Q_2 be the heat rejected from C to D at temp T_2

Then from theory of carnot engine

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

considering cycle DCEF in which Q_2 be heat absorbed and Q_3 is rejected at temp T_3.

$$\frac{Q_1}{Q_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \cdots\cdots = \text{cons.}$$

in going from a adiabatic to the other heat is either absorb or rejected. In general if Q is the amount of heat absorbed or rejected at a temp T in going from a adiabatic to other

$$\frac{Q}{T} = \text{cons.}$$

Thus const ratio is called the change in Entropy b/w the state represent by two adiabatics

Let S_1 & S_2 be resp entropy for A_1 & A_2

$S_2 - S_1 = \frac{Q}{T}$ cons

If the adiabatic are very close to each other and ds is the quantity of heat absorbed or rejected in going from one adiabatic to another.

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

Here in general the total change in entropy is going from one adiabatic to other

$$\int_{S_1}^{S_2} ds = S_2 - S_1 = \int_{A_1}^{A_2} \frac{dQ}{T}$$

The above expressions is a function of thermodynamics coordinate (P, V, T). This function is represented by symbol S and is called entropy.

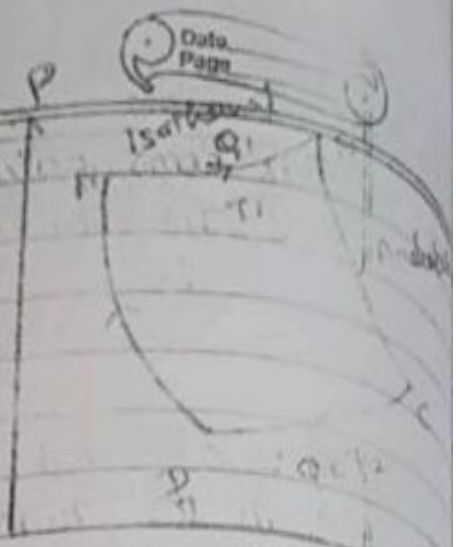
$$dQ = 0$$

So that the change in entropy $\frac{dQ}{T} = 0$

i.e., there is no change of entropy during an adiabatic process

change of entropy in a reversible process

Let us consider a reversible process shown by curve cycle ABCD in fig. In isothermal expansion A to B the working substance absorb an amount of heat Q_1 at cons temp T_1 hence gain in entropy of working substance $= \frac{Q_1}{T_1}$



During the adiabatic expansion from B to C there is no change in entropy during the Iso-thermal compression rejects a quality of heat Q_2 at cons temp T_2 of the sink.

So loss of entropy of working substance from state

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

again during the adiabatic compression D to A there is no change in entropy

Thus the net gain in the entropy of working Substance $= \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$

but, since in a complete reversal carnot cycle

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

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

i.e., in a reversible process, the total change in entropy of working substance is Zero.

Similarly the total change in combined system of Source and sink is also Zero.

Thus, in cycle of reversible process the change in entropy System is Zero. i.e

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

Change of entropy in an irreversible change

Let us consider an engine working in an irreversible process. The working substance absorbs an amount of heat Q_1 at a temp T_1 from source and rejects an amount of heat Q_2 at temp T_2 to sink. Then the efficiency of the engine is given by :-

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

Acc. to carnot theorem the efficiency is less than that of a reversible engine working b/w the same two temp T_1 & T_2.

The efficiency of reversible engine will be,

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

Acc. to carnot theorem $\eta' < \eta$

$$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

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

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

Considering the whole system the source loose the entropy by an amount Q_1/T_1 and the sink gains the entropy Q_2/T_2.

The net change in entropy for whole System

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

which is clearly +ve. Thus there is ↑ in entropy of the system during an irreversible process. The system consists of the two bodies at temp T_1 & T_2. Since heat always flows from higher to lower temp both by conduction & radiation

Let ϕ be the quantity of heat transferred from one another than ↓ in entropy of hotter body = $\frac{\phi}{T_1}$
& ↑ in entropy of colder body = $\frac{\phi}{T_2}$

therefore net ↑ in entropy of system = $\frac{\phi}{T_2} - \frac{\phi}{T_1}$

which is +ve quantity since $T_1 > T_2$ we may therefore say that the entropy of the system ↑ in all irreversible process

Principle of ↑ of entropy

The entropy of an isolated system either ↑ or remains constant as the process it undergoes are irreversible or reversible. Analytically it may be expressed as

$$\Delta S \geq 0$$

where = sign is reversible process
and > sign is irreversible process.

Thus is called principle of ↑ of entropy.

Since all physical operation in the universe are irreversible in a distant future on account of irreversibility all energy existing in diff^n forms be converted into heat energy and will not be available for conversion of mechanical work i.e. the available

energy of universe tend toward zero. It will correspond to a state of max entropy and all temp difference b/w various bodies of universe will be equalised, no heat engine will then be able do work as these state be, no heat flow from one to be possible due to the uniformity of the temp. This is called principle of degradation of energy.

Entropy and disorder

with an ↑ in entropy there is ↑ in disorder of a molecule of a substance. Thus the principle of ↑ of entropy is connected with the less ordered state of affairs. The entropy of a substance in gaseous sh is more than of liquid state bcz the molecule are more to move in gas than liquid. Moreover the entropy of the liquid state is more than in solid state bcz molecule are more free to move in liquid state.

when ice is converted into water and then into stea the entropy and disorder of molecule ↑, on other hand when the steam is converted into water & then into ice the entropy and disorder of molecule ↓.

Thus the temp of a system is lowered the amount of entropy and disorder is↓ entropy of a sys is therefore said to be a measure of degree of disorde in molecule.

2nd Law of thermodynamics

Every physical or chemical process in nature take place in such a way that there is ↑ in entropy

System due to ↑ in entropy there is ↑ in
If there is ↓ in order

At absolute zero the thermal motion completely
So that disorder and entropy tends to zero and
molecule of a substance are in perfect order
called the third law of thermodynamics.

* Nernst Heat theorem (III law of thermodynamics)

⇒ According to it the heat capacity of all solids
zero as absolute temp is approached and that
internal energy and entropy of all substance beco
equal
⇒ No entropy change takes place when pure crystalli
solid react at absolute zero.
⇒ The entropy of a solid or liquid is zero at the
zero of the temperature
i.e. there is impossibility of attending absolute z
temp

* Formulation of second law of entropy
In order to formulate the second law mathematic
Let S_A & S_B be the entropy of a substance in unit
final state A & B resp the entropy change is then g
by :-

$$S_A - S_B = \int_A^B \frac{d\varphi}{T}$$

If the two state A & B are infinitesimally clos
above eq^n may be put as $ds = \frac{d\varphi}{T}$, $\left[d\varphi = T \cdot ds\right]$

which is required mathematical formulation of second law of thermodynamics

Entropy and the second law

Acc to Kelvin Plank statement of II law there can't be perfect gas heat engine which may convert all the heat Q taken from the source at temp T into work.

If it were so entropy of source would ↓ by Q/T whereas that of working substance would remain unaltered bcz it returns to initial state after completing the cycle. Thus the entropy of system and surroundings would ↓ which is against the principle of ↑ of entropy

Acc to Clausius statement of II law there cannot be a perfect refrigerator which unaided by an external agency may transfer heat Q from a cold body at temp T_2 to hot body at temp T_1.

If it were so the entropy of cold body ↓ by Q/T_2 that of hot body would ↑ by Q/T_1 and that of working substance would remain unchanged.

Since $T_2 < T_1$ the total entropy of system & surroundings would ↓ by $Q/T_2 - Q/T_1$ which is against the principle of ↑ of entropy.

Thus the principle of ↑ of entropy is consistent with both Kelvin plank & clausius statement of II law of thermodynamics.

Thermodynamical p... & their rel^n with thermodyn... Variable (P,V,T,S)

The thermodynamical state of a system may be expr... by means of certain selected variable. These are ca... relation b/w these thermodynamical variable. The 1st law of thermodynamics provide two relations b/w them

$$dq = du + P\,dv$$

$$dq = T\,ds$$

However for complete knowledge of the system certain other relations are required and therefore these pro... we introduce some function of the variable P,V,T,S known as thermodynamical potential and thermodynam... function.

These are four thermodynamical pot^n :-

1) Initial or intrinsic energy U
2) Helmoltz's function F
3) Enthalpy or total heat H
4) Gibb's potential G

Internal or intrinsic energy.

From 1st law of thermodymics

$$du = dq - dw$$

$$du = dq - P\,dv$$

From 2nd law of thermodymics

$$dq = T\,ds$$

$$\boxed{du = T\,ds - P\,dv}$$

Here internal energy is one of the thermodynamic potential relating P, V, T, S are given above table partial derivatives of internal energy w.r.t to vari s.t V

$$\left[\frac{du}{ds}\right]_{V\,cons} = T$$

$$\left[\frac{du}{dV}\right]_S = -P$$

Now since du is perfect differential we must hav

$$\frac{\partial}{\partial V}\left[\frac{\partial u}{\partial s}\right]_V = \frac{\partial}{\partial s}\left[\frac{\partial u}{\partial V}\right]_S$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial s}\right)_V} \quad -(1)$$

This is known as Maxwell first thermodynamical Re

2) Helmholtz's function F

From the first law & second law of thermodynam

$$du = T\,ds - dw$$

If we consider process in which the system exchange heat with surrounding and is thirty maintained at a cons temp T, then

$$T\,ds = d(TS) \text{ and we may write}$$

$$du = d(TS) - dw$$

$$d(u - TS) = -dw$$

$$\boxed{dF = -dw}$$

where $F = (U - TS)$ is known as "Helmholtz free energ

differentiating F we get

$$dF = du - d(TS)$$

$$dF = du - T\,ds - S\,dT$$

but $dU = T\,ds - P\,dV$

$$dF = -(P\,dV + S\,dT)$$

Here T & V are independent variable taking partial

$$\left[\frac{\partial F}{\partial V}\right]_T = -P \quad ; \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$$

Since dF is a perfect differential we may write

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad -(4)$$

This is known as Maxwell's second thermodynamical eq.

3) Enthalpy or total heat 'H'.

The function enthalpy is defined as $H = U + PV$ differentiate of it

$$dH = dU + P\,dV + V\,dP$$

$$= T\,dS - P\,dV + P\,dV + V\,dP$$

$$dH = T\,dS + V\,dP$$

At cons pressure $dH = T\,dS = dQ \quad (\because dP = 0)$

i.e for an isobaric process change in enthalpy is equal to heat given to system

Here S & P are independent variable taking partial differential of H wrt P & S

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad ; \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dH is perfect differential we may write

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Gibbs's Potential 'G'

From defenation of enthalpy

$$H = U + PV$$

$$dH = du + Pdu + Vdp$$

$$= T\,ds - P\,dv + Pdv + vdv$$

$$dH = T\,ds - P\,dv$$

If the process be isothermal isobaric as isochoric

$$T\,ds = d(TS) \quad \text{or } dP = 0$$

$$dH = d(TS)$$

$$d(H - TS) = 0$$

$$dG = 0$$

$$G = H - TS = \text{cons}$$

Now, $G = H - TS$

$$G = U + PV - TS \qquad \because f = U - TS$$

$$G = F + PV$$

Now differentiating G ... wrt ...

$$dG = du + d(PV) - d(TS)$$

$$dG = du + pdv + vdp - Tds - SdT$$

$$dG = vdP - SdT \rightarrow (Tds)$$

Here undependent variables are P & T, taking partially differential of G wrt P & T

$$\left(\frac{\partial G}{\partial P}\right)_T = V \; ; \quad \left(\frac{\partial G}{\partial P}\right)_P = -S$$

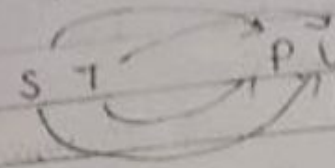
Since dG is perfect differential, we may write

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \quad \text{---(4)}$$

This is known as Maxwell's forth thermodynamical relation

we see that four thermodynamical potentials $U(S,V)$, $F(T,V)$, $H(S,P)$, $G(T,P)$ lead us to four thermodynamical relation known as Maxwell Rel^n



I. $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

II. $\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial P}{\partial T}\right)_V$

III. $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$

IV. $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

- Equilibrium of thermodynamic system

A system at cons. temp. and volume is in state of equilibrium when Helmoltz free energy F is minimum.

$$F = U - TS$$

$$dF = dU - d(TS)$$

$$dF = T\cdot dS - P\cdot dV - T\cdot dS - S\cdot dT$$

$$dF = -P\cdot dV - S\cdot dT$$

in an isothermal or isochoric process

$$dV = 0,\ dT = 0$$

$$\text{if then } dF = 0 \qquad \boxed{F = F_{min}}$$

Similarly system at cons temp and pressure will be in equilibrium

when Gibbs pot^n (G) is minimum

$$G = H - TS$$

$$G = U + PV - TS$$

$dG = T\,ds - p\,dv$ (or) $dG = v\,dp - s\,dT$

In a isothermal equilibrium process $dG = 0$ [G = Gibbs]

Clausius Clayperon's eq^n

From Maxwell's II thermodynamic rel^n

$$\left[\frac{\partial p}{\partial T}\right]_V = \left[\frac{\partial s}{\partial v}\right]_T$$

multiplying both sides

$$T\left[\frac{\partial p}{\partial T}\right]_V = T\left[\frac{\partial s}{\partial v}\right]_T$$

$$T\left[\frac{\partial p}{\partial T}\right]_V = \left[\frac{\partial Q}{\partial v}\right]_T$$

from II law of thermodynamics $\partial Q = T\,\partial s$

These right hand side of the above eq^n represents the quantity of heat absorbed or liberated per unit change in volume at const temp T.

i.e at const temp the quantity of heat liberated must be latent heat and change in volume during change of state

considering a unit mass of substance. Let L be the latent heat when the substance changes at const temp T from V_1 to V_2 then

$$\partial Q = L \quad \& \quad \partial v = V_2 - V_1$$

$$L = (V_2 - V_1)\,T\left[\frac{\partial p}{\partial T}\right]$$

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \quad \text{--- (1)}$$

This is clausius – clayperons latent heat eqn

Effect of pressure on boiling point of liquid

When a liquid boils i.e changes from liquid state to gaseous state. There is an ↑ in its volume.

So that $V_2 > V_1$, $V_2 - V_1$ is +ve

hence from eqn (1) dp/dT will also be a +ve quantity i.e the boiling point of liquid rise with ↑ in pressure & vice versa.

Effect of pressure on melting point of solid

When a solid melts there may be an ↑ in volume in substance like wax and vapour or there may be ↓ in volum of substance like galium, ice, Bismith.

when $V_2 > V_1$, $V_2 - V_1$ is +ve

Here dp/dt will be +ve quantity i.e melting point of such substance rises with ↑ in pressure

when $V_2 < V_1$, $V_2 - V_1$ is -ve

Here dp/dt will be -ve quantity i.e m.p of such substance decreases ↓ in pressure

Joulson Expansion

Joule Thomson expansion: the enthopy of n moles of gas

$H = U + pV$

$dH = dU + Vdp + pdV = 0$

$dH = dU + pdV + Vdp = 0$

$dH = TdS + Vdp$ --- (1)

Consider the entropy 'S' as a function of the independent variable P & T, $S = S(P,T)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Substituting above value of dS in eqn (1)

$$T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP + V dP = 0 \quad (2)$$

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$$

from maxwell forth thermodynamical relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Therefore eqn (2) becomes

$$C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP + V dP = 0$$

$$C_P dT = dP\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] = 0$$

Joule Thomson coefficient $\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]}$ (3)

Change of temperature during adiabatic process

From Maxwell's first law :- $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)$

On multiplying & dividing T on right hand side

$$\left(\frac{\partial T}{\partial S}\right) = \frac{T}{T}\left(\frac{\partial P}{\partial S}\right)_V = -T\left(\frac{\partial P}{\partial S}\right)$$

since in ↑ in amount of heat at const. Volume always results in an ↑ of pressure therefore the term $\left(\frac{\partial P}{\partial Q}\right)_V$ is +ve hence the term $\left(\frac{\partial T}{\partial V}\right)_S$ is -ve.

i.e the temp should ↓ with an ↑ in Volume under condition of cons entropy in other words the adiabatic expansion must result in fall of temp.

from Maxwell's III thermodynamical relation

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

On multiplying and dividing by T on R.H.S.

we get $\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial Q}\right)_P$

Since an ↑ in quality of heat at cons pressure always results in an ↑ in volume. Therefore the term $\frac{\partial V}{\partial Q}$ is +ve hence $\left(\frac{\partial T}{\partial P}\right)_S$ is also +ve.

i.e temp must ↑ with ↑ in pressure under condition of cons entropy.

In other words in adiabatic compression temp must rises.

Cooling by adiabatic demagnetisation

In the process of magnetizing a substance there is work done on substance in aligning the elementary magnet in direction of magnetic field. This work done is store in substance in form of magnetic energy.

If the magnetic substance is demagnetised adiabatically at its temp. ... fase and versa ... [illegible]

There is drop in temp of substance the drop in temp due to adiabatic demagnetisation is called magnetic caloric effect.

When a paramagnetic is placed in magnetising field it's elementary magnetic dipole get aligning in the direction of field.

The magnetic moment per unit volume thus caused "Intensity of magnetisation"

Acc to curie law, "the magnetic susceptibility is inversely proportional to absolute temp

$$\chi \propto \frac{1}{T}$$

$$\chi = \frac{C}{T} \quad -(A) \qquad \{C = \text{curie const}$$

$$\chi = \frac{I}{H} \quad -(B)$$

from A & B $\quad \frac{C}{T} = \frac{I}{H} \Rightarrow I = C\left[\frac{H}{T}\right] \quad -(1)$

If V be molar volume then intensity of magnetisation of one mole of substance

$$M = IV$$

$$M = C\left[\frac{H}{T}\right]V = \frac{CVH}{T} \quad -2$$

Let us now suppose that one mole of paramagnetic substance is placed in magnetising field then it's thermodynamic behaviour can be expressed in terms of thermodynamical variable P, V, T. But in thermodynamical [illegible]

whereas there an ↑ in H results in ↑ in M therefore replacing p by -H & V by +M in maxwell third relation

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-(\partial M/\partial T)_H}{(\partial S/\partial T)_H} = \frac{-T(\partial M/\partial T)_H}{T(\partial S/\partial T)_H}$$

$$= \frac{-T(\partial M/\partial T)_H}{(\partial Q/\partial T)_H}$$

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H \quad -(3)$$

from eqⁿ (3)

specific heat of substance ... const magnetising field ... (adiabatic)

$$\boxed{dT = \frac{-T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H dH}$$

for a finite change of field from H_1 to H_2 the change in temp will be

$$\Delta T = -\frac{T}{C_H}\int_{H_1}^{H_2}\left(\frac{\partial M}{\partial T}\right)_H dH$$

differentiating eqⁿ (2) w.r.t. to T at cons H

$$\left(\frac{\partial M}{\partial T}\right)_H = -\frac{CV}{T^2} H$$

$$\therefore \Delta T = -\frac{T}{C_H}\left(\frac{-CV}{T^2}\right)\int_{H_1}^{H_2} dH$$

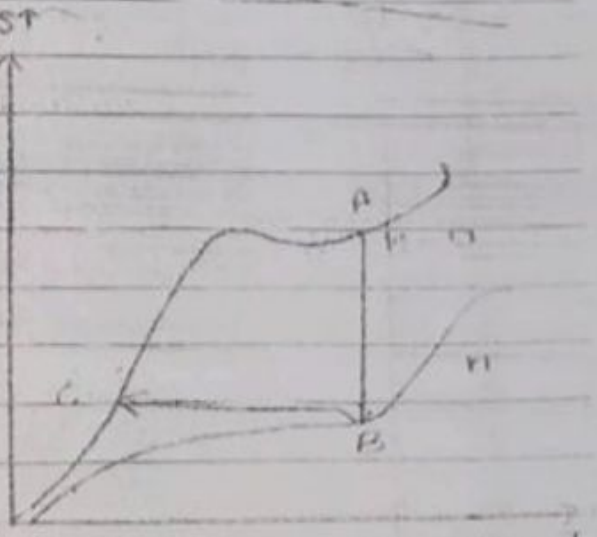
$$\Delta T = \frac{1}{2}\frac{C_V}{C_H T}\left[H_2^2 - H_1^2\right] \quad -(3)$$

If the magnetic field is reduced from H to 0 ($H = H_1 = H_2$ & $H_2 = 0$) then change in temp is given by –

$$\Delta T = \frac{-C_V}{2C_H T} \times H^2 \quad -(4)$$

from eqn (4) we see that temp of paramagnetic solid ↓ as the field is reduced ∴ greater is the initial field H & lower the initial temp T greater is temp drop ΔT

- Temp and entropy diagram



The change in entropy during isothermal magnetisation is represented by ↓ AB this shows that during magnetisation the entropy of a substance ↓ now the field is switched off the substance demagnetised adiabatically. So the temp of substance falls while entropy remains cons which is shown by arrow BC

Ratio of adiabatic and isothermal

$$E = \frac{\text{Stress}}{\text{Volume strain}} = \frac{-dp}{dv/v} = -\frac{v\,dp}{dv}$$

$E_S = -V\left[\frac{\partial P}{\partial V}\right]_S$ -ve Sign due to ↑ in temp there is ↓ in volume & vice versa

$$E_T = -V\left[\frac{\partial P}{\partial V}\right]_T$$

Now $\frac{E_S}{E_T} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T} = \frac{(\partial P/\partial T)_V (\partial T/\partial V)_S}{(\partial P/\partial T)_V (\partial T/\partial V)_T}$

- from Maxwell's III relⁿ $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$

from I relⁿ $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P$

from IV relⁿ $\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$

from II relⁿ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Substituting above values in eqn(1)

$$\frac{E_S}{E_T} = \frac{(\partial S/\partial V)_P (\partial P/\partial S)_V}{(\partial T/\partial V)_P (\partial P/\partial T)_V}$$

$$= \left(\frac{\partial S}{\partial V} \cdot \frac{\partial V}{\partial S}\right)_P \times \left(\frac{\partial P}{\partial T} \times \frac{\partial T}{\partial P}\right)_V$$

$$= \left(\frac{\partial S}{\partial T}\right)_P \times \left(\frac{\partial T}{\partial S}\right)_V$$

$$= \frac{(\partial Q/\partial T)_V}{(\partial Q/\partial S)_V} = \frac{C_V}{C_P}$$

$$\boxed{\frac{E_S}{E_T} = \frac{C_V}{C_P}}$$

T·ds Equations

first T·ds eqⁿ

If the entropy s of a thermodynamic system is function of T and v. Then,

$$S = S(T, v)$$

$$ds = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial V}\right)_T dv$$

$$T \cdot ds = T\left(\frac{\partial S}{\partial T}\right)_v dT + T\left(\frac{\partial S}{\partial v}\right)_T dv$$

$$T\left(\frac{ds}{\partial T}\right)_v = \frac{\partial Q}{\partial T} = C_v$$

from Maxwell's Second relⁿ ⇒ $\boxed{T \cdot ds = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv}$

Second T·ds eqⁿ

If the entropy S of a thermo. System is a function of T & P then $S = S(T, P)$

$$ds = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$T\,ds = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$T\left(\frac{\partial S}{\partial T}\right) = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$$

and maxwell's IV relⁿ $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$\boxed{T\,ds = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP}$$

• Prove the Gibbs Helmholtz eqn

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V\right]$$

Soln

$$F = U - TS$$

$$dF = dU - d(TS) \Rightarrow dU - T\cdot dS - S\cdot dT$$

$$= TdS - P\cdot dV - T\cdot dS - S\cdot dT$$

$$dF = -P\,dV - S\cdot dT \quad -(1)$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad -(2)$$

from (1) & (2)

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V$$

$$\boxed{U = F - T\left(\frac{\partial F}{\partial T}\right)_V}$$

$$\frac{\partial}{\partial T}\left(-\frac{F}{T}\right)_V = -\frac{F}{T^2} + \frac{1}{T}\left(\frac{\partial F}{\partial T}\right)_V$$

$$\frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V = \frac{-F + T\left(\partial F/\partial T\right)_V}{T^2}$$

$$-T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

$$\boxed{-T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V\right] = F - T\left(\frac{\partial F}{\partial T}\right)_V = U}$$