



Thermodynamics And Statistical Physics

A. Thermodynamics

5-chapter

unit-I

(1, 2, 3)

unit-II

(4, 5)

B. Statistical Physics

unit-III

(6)

unit-IV

(7)

UNIT-I

→ Chapter-1 Thermal and Adiabatic interaction and Basic concepts of Thermodynamics.

→ Chapter-2 Heat Engine, second law of Thermodynamics and their Applications.

→ Chapter-3 General interaction of Thermodynamics. [Phase transition, Maxwell's equation and their Application, Claudius-Clayperon Equation]

UNIT-II

→ Chapter-4

Production of low temperature and Helium-I

i. and Helium-II.

→ Chapter-5 The distribution of molecular velocities and transport phenomenon.

UNIT-III

→ Chapter-6 Classical statistical → Maxwell Boltzmann (MB)

UNIT-IV

→ Chapter-7 Quantum statistical → A) Fermi Dirac statistical
B) Bose Einstein statistical

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Dr. Lokesh Kumar Jangir



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Chapter - 1

Macro and Micro System

Thermodynamics & statics Physics (7 chapter)

(A) Thermodynamics

[1, 2, 3, 4, 5]

Ch. 1, 2, 3 UNIT-I

Ch. 4, 5 UNIT-II

Ch. 6 UNIT-III

Ch. 7 UNIT-IV

(B) Statics Physics

[6, 7]

A. Thermodynamics Physics

That branch of Physics by which relation can be find between external parameters, is said to be thermodynamics.

External Parameter :- The factor that change state of matter is said to be external parameter.

for example - Pressure (P), Temperature (T), Area (A) etc.

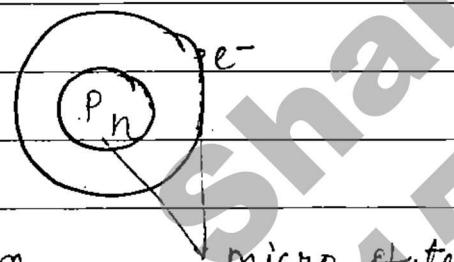
(B) Statics Physics :- That branch of physics by which relation can be find between micro and macro state is said to be statics physics.

Macro system and Micro system - That system in which

particals are present in majority, is said to be macro system.

And the present particals in this are called micro system.

Example:- atom is a macro system and electron, proton, neutron are micro system.



Atom
(macro state)

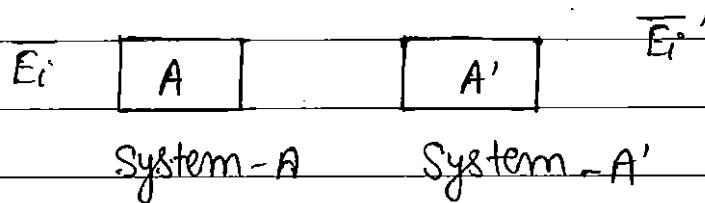
micro state

We know that, micro state is connected to the energy level and energy level are connected to quantum number. therefore we can say that micro state is connected to the quantum numbers.

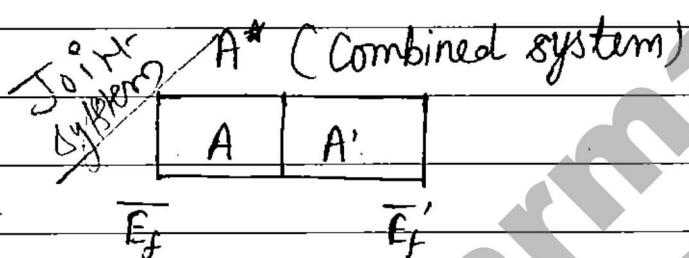
NOTE:- In the thermodynamics physics, internal structure of matter is not studied.

I. Interaction of Macro System :-

- ① When system do not put in contact of heat -



- ⑥ When system is placed in heat contact



Let there are two macro system A and A'. When both systems do not placed in heat contact then average energy of A-system is \bar{E}_i and average energy of system - A' is \bar{E}_i' . Now, both macro system are placed in heat contact. Due to interaction, exchange of heat takes place between both system. Suppose average energy of system A is \bar{E}_f and average energy of system A' is \bar{E}'_f . Both of these system make a combined system. Suppose this combined system is A^* . According energy conservation law total energy of combined system A^* should be constant. from energy conservation law -

Total average energy before interaction =
Total energy after interaction

$$\bar{E}_i + \bar{E}_{i'} = \bar{E}_f + \bar{E}'_f$$

$$\bar{E}_f - \bar{E}_i + \bar{E}'_f - \bar{E}'_i = 0$$

$$[\Delta \bar{E} + \Delta \bar{E}' = 0] \quad \text{--- } ①$$

Where, $\Delta \bar{E}$ = Change in average energy for system - A

$\Delta \bar{E}'$ = change in average energy for system - A'

It is clear from eq. ① that change occurs in average energy of both system. On the basis of this change in energy there are two types of interaction -

(i) Thermal Interaction

(ii) Adiabatic Interaction

(i) Thermal Interaction :- That thermal interaction in which external parameters (P, V, A, T) remain constant and exchange of heat take place, is called Thermal interaction.

(ii) Adiabatic Interaction :- The interaction in which external parameters (P, V, A, T) are not constant and exchange of heat does not take place, is called adiabatic interaction.

* * *
(iii)

General Interaction:- The interaction in which exchange of heat take place and external parameters (P, T, A) do not remain constant, is called general interaction.

Mostly, interaction happen in universe, is called general interaction. General interaction satisfies energy conservation law which first law of thermodynamics

from first law of thermodynamics -

$$dQ = dU + dW$$

$$\therefore dW = PdV$$

HTIP

$$dQ = dU + PdV \quad \textcircled{1}$$

Where,

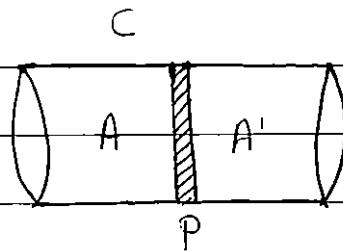
dQ = Total energy of system

dU = Internal energy of system

$dW = PdV$ = Work-energy (Pressure-volume energy)

According to first law of thermodynamics, "Total energy of system is equal to sum of internal energy of system and pressure volume energy".

Now we explain these interactions by an example



To explain interaction we imagine a hollow cylinder. In this hollow cylinder two type of gass A and A' are filled. A piston is arranged in the cylinder to seprate both the gasses.

- 1: If piston is not made up of thermal insulator matter and it is present in rest state, then interaction take place in cylinder will be thermal interaction. Because, in the hollow cylinder exchange of heat take place and external parameters are constant.
- 2: If piston is made up of thermal insulator matter and it is ^{not} present in rest state, then interaction taking place in the cylinder will be adiabatic interaction. Because, exchange of heat do not take place and external parameters are not constant.
- 3: If piston is not made up of thermal insulator matter and it is in moving state then the interaction taking place is general interaction.

Because in the hollow cylinder exchange of heat takes place and external parameters are not constant.

1. Helmholtz Energy :- In the thermodynamics physics, work done by isothermal system is defined by an energy. This energy is known as Helmholtz energy. Helmholtz energy is denoted by 'F'.

So, Helmholtz energy -

$$\text{M.T.P} \quad F = U - ST$$

where,

U = Internal energy

S = Entropy

T = Temperature

F = Helmholtz energy

Proof :- We know that, from the first law of thermodynamics

$$dQ = dU + dW \quad \dots$$

$$-dW = dU - dQ \quad \dots \textcircled{1}$$

from the second law of thermodynamics

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

$$dQ = T dS \quad \text{--- } (2)$$

by put the value in eq.① from eq.②

$$-dW = dU - T dS \quad \text{--- } (3)$$

Now $d(ST) = SdT + TdS$

from the definition of Helmholtz energy

$T = \text{constant} = \text{for isothermal system}$

$$dT = 0$$

put the value

$$d(ST) = TdS \quad \text{--- } (4)$$

by substituting value in eq.③ from eq.④

$$d(-W) = dU - d(ST)$$

$$d(-W) = d(U - ST)$$

by integrating

$$-W = U - ST \quad \text{--- } (5)$$

work done by isothermal system is equivalent to helmholtz energy

$$\therefore -W = F$$

from eq.n (5)

$$F = U - ST$$

Q. Enthalpy :- If value of pressure is constant on system (isobaric system) then, total energy of system is said to be enthalpy in thermodynamics physics. Enthalpy is represented by 'H'.

So, enthalpy of system :

M.T.R.

$$H = U + PV$$

Proof :- If volume of any system is constant then pressure volume energy of that system is zero. i.e. value of work done by system is zero.

from the first law of thermodynamics,

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

$$\therefore dW = PdV$$

by put the value in eq. (1)

$$dQ = dU + PdV \quad \text{--- (2)}$$

$$\because V = \text{Constant}$$

to write in differentiate form

$$dV = 0$$

by substituting value of dV in eq. (2)

$$dQ = dU$$

by integration ***

$$Q = U \quad \text{--- (3)}$$

so it is clear from eq.(3) that volume of system is constant then total energy (Q) of system, is equivalent to internal energy (U) of system.

If pressure of system is constant then suppose, in the initial position volume and internal energy of system is V_1 and U_1 respectively and in final position volume and internal energy of system is V_2 and U_2 respectively.

from eqn (3)

$$dQ = dU + PdV$$

$$dQ = (U_2 - U_1) + P(V_2 - V_1)$$

$$dQ = U_2 - U_1 + PV_2 - PV_1$$

$$dQ = (U_2 + PV_2) - (U_1 + PV_1)$$

from definition of enthalpy

$$H_2 = U_2 + PV_2 = \text{Total energy of system in final position}$$

$$H_1 = U_1 + PV_1 = \text{Total energy of system in initial position}$$

put values,

$$dQ = H_2 - H_1$$

$$dQ = dH$$

on integrating

$$Q = H \quad \text{--- (5)}$$

It is clear from eq. (5) that total energy of system is called enthalpy.

so, enthalpy in general form

$$H = U + PV$$

* * 3: Gibbz free Energy :- In thermodynamics physics at the constant temperature and pressure, the work done by system extra than pressure-volume energy (dW), is defined in the form of energy. This energy is called gibbz free energy.

It is denoted by ' G_f '

so, gibbz free energy,

H.T.P

$$G_f = U + PV - ST$$

* ↑ or

$$G_f = H - ST$$

* *

or

$$G_f = F + PV$$

where,

U = Internal energy of system

P = Pressure

T = Temperature

S = Entropy

V = Volume of system

H = Enthalpy

F = Helmholtz Energy

G = Gibbs free energy

Proof :- We know that from the first law of thermodynamics

$$dQ = dU + dW$$

$$\therefore dW = PdV \quad (\text{pressure-volume energy})$$

$$dQ = dU + PdV \quad \textcircled{1}$$

correct form of first law -

$$dQ = dU + dW + dWe$$

$$-dWe = dU + dW - dQ \quad \textcircled{2}$$

From the second law of thermodynamics

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

$$dQ = TdS \quad \textcircled{3}$$

$$\therefore dW = PdV$$

by substituting values in eq. ② from eq. ③

$$-dW_e = dU + PDV - TdS$$

From the property of differential operator

$$d(-W_e) = dU + d(PV) - d(ST)$$

$$d(-W_e) = d(U+PV - ST)$$

on integrating above equation

$$-W_e = U + PV - ST$$

from the definition of Gibbs free energy

$$-W_e = G$$

on putting values

$$\boxed{G = U + PV - ST} \quad \text{--- } ④$$

From definition of enthalpy,

$$H = U + PV$$

put the value in eq. ④

$$\boxed{G = H - ST} \quad \text{--- } ⑤$$

From definition of Helmholtz energy

$$F = U - ST \quad \text{--- } ⑥$$

from eq. ⑥ and ④

$$\boxed{G = F + PV} \quad \text{--- } ⑦$$

~~QNA~~ • Gibbz - Helmholtz Equation

We know that,
from definition of Gibbz free energy

$$G = U + PV - ST$$

to write in differential form

$$dG = dU + d(PV) - d(ST)$$

$$dS = dV + PdV + VdP - SdT - TdS \quad \text{--- (1)}$$

From definition of first law of thermodynamics

$$dQ = dU + dW$$

$$\therefore dW = PdV \quad (\text{Pressure volume energy})$$

by put the value

$$dQ = dU + PdV \quad \text{--- (2)}$$

From second law of thermodynamics

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

$$dQ = TdS \quad \text{--- (3)}$$

from eq. 1 (2) and (3)

$$TdS = dU + PdV \quad \text{--- (4)}$$

by substituting value in eq. 1 from eq. 4

$$dG = Tds + Vdp - SdT - Tds$$

x**

$$dG = Vdp - SdT \quad \text{--- (5)}$$

Case-I P_f $P = \text{constant}$
by differentiating
 $dp = 0$
from eq.n (5)

$$dG = -SdT$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P=\text{const.}} \quad \text{--- (6)}$$

$$\therefore G = U + PV - ST$$

put the value from eq. (6)

$$G = U + PV + T \left(\frac{\partial G}{\partial T}\right)_{P=\text{constant}}$$

from the \rightarrow Enthalpy

$$H = U + PV$$

by put the value

$$G = H + T \left(\frac{\partial G}{\partial T}\right)_{P=\text{constant}} \quad \text{--- (7)}$$

Case-II T_f Temperature $T = \text{constant}$

by differentiation

$$\frac{dG}{dT} = 0$$

from eq. n ⑤

$$dG_1 = V dP$$

$$V = \left(\frac{\partial G_1}{\partial P} \right)_{T=\text{Const.}} \quad \text{--- ⑥}$$

$$\therefore G_1 = U + PV - ST$$

by putting value from eq. ⑧

$$G_1 = U - ST + P \left(\frac{\partial U}{\partial P} \right)_{T=\text{Const.}} \quad \text{--- ⑨}$$

from the definition of Helmholtz energy

$$F = U - ST$$

but the value

$$G_1 = F + P \left(\frac{\partial G}{\partial P} \right)_{T=\text{Constant}} \quad \text{--- ⑩}$$

Equation ⑦ and ⑩ are called Gibbs - Helmholtz equation.

Eq. n ⑦ is Gibbs - Helmholtz equation in the form of enthalpy (H) and eq. ⑩ is called Gibbs - Helmholtz equation in the form of Helmholtz energy (F)

- Maxwell's Equation :- In the thermodynamics physics, there are four thermodynamic coordinates. Thermodynamic coordinates are denoted by P, V, T, S.
The equation which reveals relation among thermodynamic coordinates, is called Maxwell's equation.
In the thermodynamics there are four energy functions. These energy functions are denoted by U, F, G, H.
Maxwell equations are find by energy functions. In thermodynamics, Maxwell has given four equations.

First equation of Maxwell -

We know that,
From the first law of thermodynamics

$$dQ = dU + dW$$

$$\therefore dW = PdV \quad (\text{Work energy})$$

on putting values

$$dQ = dU + PdV \quad \dots \quad (1)$$

Again we know that,

from second law of thermodynamics -

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

$$dQ = Tds \quad \text{--- (2)}$$

from eq. (1) and (2)

$$Tds = dU + pdV$$

$$dU = Tds - pdV \quad \text{--- (3)}$$

Case-I

If $V = \text{constant}$
to write in differential form

$$dV = 0$$

from eq. (3)

$$dU = Tds$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{--- (4)}$$

Differentiate with respect to V , $S = \text{constant}$

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)\right]_{V=\text{const.}, S=\text{const.}} = \left(\frac{\partial T}{\partial V}\right)_{S=\text{const.}} \quad \text{--- (5)}$$

Case-II

If $S = \text{constant}$

to write in differential form

$$dS = 0$$

from eq. (3)

$$dU = -pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_{S=\text{const.}} = -p \quad \text{--- (6)}$$

Differential with respect to S , $V = \text{Const}$.

$$\left[\frac{\partial}{\partial S} \left(\frac{\partial V}{\partial V} \right)_{S=\text{Const.}} \right]_{V=\text{Const.}} = - \left(\frac{\partial P}{\partial S} \right)_{V=\text{Constant}} \quad (7)$$

By the property of differential operator

$$\therefore \frac{\partial^2 f}{\partial x \partial f} = \frac{\partial^2 f}{\partial y \partial x} \quad (8)$$

From eqn (5), (7) & (8), we have

M.T.R.

$$\left[\left(\frac{\partial P}{\partial S} \right)_{V=\text{Const.}} \right] = - \left(\frac{\partial T}{\partial V} \right)_{S=\text{Const.}}$$

above equation is termed as Maxwell's first equation.

Q. Second Equation of Maxwell :-

We know that,
from the Helmholtz energy

$$F = U - ST$$

To write in differential form

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

$$dF = dU - Tds - SdT \quad (1)$$

Again, we know that
from first law of thermodynamics

$$dQ = dU + PdV \quad \text{--- (2)}$$

from second law of thermodynamics

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

$$dQ = Tds \quad \text{--- (3)}$$

from eqn (2) and (3)

$$Tds = dU + PdV \quad \text{--- (4)}$$

by substituting value in eq. (1) from eq. (4)

$$df = dU - dU - PdV - SdT$$

$$\boxed{df = -PdV - SdT} \quad \text{--- (5)}$$

Case-I

if $V = \text{Constant}$
to write in differential form

$$dV = 0$$

from eq. (5)

$$dF = -SdT$$

$$\left(\frac{\partial F}{\partial T} \right)_V = -S \quad \text{--- (6)}$$

Dif. with r to N , $T = \text{Constant}$

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V \right]_T = - \left(\frac{\partial S}{\partial V} \right)_T \quad \text{--- (7)}$$

Case-II If $T = \text{Constant}$

to write in differential form

$$dT = 0$$

from eq.n (5)

$$dF = -PdV$$

$$\left(\frac{\partial F}{\partial V} \right)_{T=\text{Const.}} = -P \quad \text{--- (8)}$$

Diff. with respect to T , $V = \text{Constant}$

$$\left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T \right]_V = - \left(\frac{\partial P}{\partial T} \right)_{V=\text{Const.}} \quad \text{--- (9)}$$

From the property of differential operator

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad \text{--- (10)}$$

from eq.(7), (9) and eq.(10)

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

Above equation is second equation of Maxwell.

3. Third Equation of Maxwell :-

We know that,
from the definition of enthalpy

$$H = U + PV$$

to write in differential form

$$dH = dU + P(dV)$$

$$dH = dU + PDV + VdP \quad \textcircled{1}$$

From first law of thermodynamics

$$dQ = dU + PDV \quad \textcircled{2}$$

From second law of thermodynamics

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

$$dQ = TdS \quad \textcircled{3}$$

from eq.n $\textcircled{2}$ and $\textcircled{3}$

$$TdS = dU + PDV \quad \textcircled{4}$$

by substituting value in eq. $\textcircled{1}$ from $\textcircled{4}$

$dH = TdS + VdP$	—	$\textcircled{5}$
------------------	---	-------------------

Case-I if $S = \text{constant}$

to write in differential form

$$dS = 0$$

from eq. ⑤

$$dH = Vdp$$

$$\left(\frac{\partial H}{\partial p}\right)_{S=\text{const.}} = V \quad \text{--- } ⑥$$

Dif. with respect to S , $P = \text{constant}$

$$\left[\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial p} \right)_{S=\text{const.}} \right]_{P=\text{const.}} = \left(\frac{\partial V}{\partial S} \right)_{P=\text{const.}} \quad \text{--- } ⑦$$

Case-II If $P = \text{constant}$

to write in differential form,

$$dp = 0$$

from eq. ⑤

$$dH = Tds$$

$$\left(\frac{\partial H}{\partial s}\right)_{P=\text{const.}} = T \quad \text{--- } ⑧$$

Dif. with respect to p , $S = \text{constant}$

$$\left[\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial s} \right)_{P=\text{const.}} \right]_{S=\text{const.}} = \left(\frac{\partial T}{\partial p} \right)_{S=\text{const.}} \quad \text{--- } ⑨$$

By the property of differential operator

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad \text{--- (10)}$$

from eq. (7), (9) and (10)

$$\left| \frac{(\partial V)}{(\partial S)} \right|_{P=\text{const.}} = \left| \frac{(\partial T)}{(\partial P)} \right|_{S=\text{const.}}$$

Above equation is called third eq. of Maxwell.

- Fourth Equation of Maxwell :-

We know that,
from the definition of Gibbs free energy -

$$G = U + PV - ST$$

to write in differential form,

$$dG = dU + d(PV) - d(ST)$$

$$dG = dU + PdV + VdP - SdT - TdS \quad \text{--- (1)}$$

From, first law of thermodynamics

$$dQ = dU + PdV \quad \text{--- (2)}$$

From, second law of thermodynamics

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

$$dq = Tds \quad \text{--- (3)}$$

from eq. (2) and (3)

$$Tds = dU + pdV \quad \text{--- (4)}$$

by substituting value in eq. (1) from (4)

$$dG = Tds + Vdp - SdT - Tds$$

$$\boxed{dq = Vdp - SdT} \quad \text{--- (5)}$$

Case-I If $P = \text{constant}$

to write in differential form

$$dp = 0$$

from eq. (5)

$$dq = -SdT$$

$$\left(\frac{\partial q}{\partial T}\right)_{P=\text{Const.}} = -S \quad \text{--- (6)}$$

diff. with respect to P , when $T = \text{constant}$

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial q}{\partial T} \right)_{P=\text{Con.}} \right]_{T=\text{Con.}} = - \left(\frac{\partial S}{\partial P} \right)_{T=\text{Con.}} \quad \text{--- (7)}$$

Case-II If $T = \text{constant}$

To write in differential form

$$dT = 0$$

from eq. ⑤

$$dQ = V dp$$

$$\left(\frac{\partial Q}{\partial P} \right)_{T=\text{Const.}} = V \quad \text{--- } ⑥$$

Dif. with respect to T, P = Const.

$$\left[\frac{\partial}{\partial T} \left(\frac{\partial Q}{\partial P} \right)_{T=\text{Const.}} \right]_{P=\text{Const.}} = \left(\frac{\partial V}{\partial T} \right)_{P=\text{Constant}} \quad ⑦$$

From the property of differential operator

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad ⑧$$

Now, from eq. ④, ⑥, ⑧

$$\boxed{- \left(\frac{\partial S}{\partial P} \right)_{T=\text{Const.}} = \left(\frac{\partial V}{\partial T} \right)_{P=\text{Const.}}}$$

Above equation is known as fourth equation of Maxwell.

Maxwell's equation are -

$$+ \left(\frac{\partial P}{\partial S} \right)_{V=\text{Con.}} = - \left(\frac{\partial T}{\partial V} \right)_{S=\text{Con.}}$$

$$\star \star \underline{2.} \quad \left(\frac{\partial S}{\partial V} \right)_{T=\text{Con.}} = \left(\frac{\partial P}{\partial T} \right)_{V=\text{Con.}}$$

$$\underline{3.} \quad \left(\frac{\partial V}{\partial S} \right)_{P=\text{Con.}} = \left(\frac{\partial T}{\partial P} \right)_{S=\text{Con.}}$$

$$\star \star \underline{4.} \quad + \left(\frac{\partial S}{\partial P} \right)_{T=\text{Con.}} = - \left(\frac{\partial V}{\partial T} \right)_{P=\text{Con.}}$$

- Application of Maxwell's Equation -

Clausius - Clapeyron Equation This equation is find by maxwell's equation. That's why this equation is called application of maxwell equation.

Proof: We know that,

from the second equation of Maxwell

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

Multiply by T in both sides

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

$$\left(-\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{--- (1)}$$

again we know that
from second law of thermodynamics

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

to write in partial differential form

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

$$dQ = T dS \quad \text{--- (2)}$$

by put the value in eq. (1)

$$\left(\frac{\partial Q}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{--- (3)}$$

Latent Heat :- Change in the heat of system
at the constant temperature
is said to be latent heat. (respect to volume)
It is represented by L' .

Let us consider that volume
of system in the initial state is V_1 and in
the final state it is V_2 . so change in volume
of system

$$dV = V_2 - V_1$$

from definition of latent heat.

$$\left(\frac{\partial Q}{\partial V}\right)_T = \frac{L}{V_2 - V_1} \quad \text{--- (4)}$$

from eq.n ③ & ④

$$T \left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{V_2 - V_1}$$

H.T.R:

$$\left[\left(\frac{\partial P}{\partial T}\right)_V = \frac{L}{T(V_2 - V_1)}\right] \quad \text{--- (5)}$$

Equation ⑤ is known as Clausius-Clapryean eq.

* * * 2. Joule-Thomson coefficient Value :- In the Joule-Thomson experiment value of enthalpy remains constant. it is principle of Joule-thomson experiment. Joule-Thomson coefficient is denoted by M_H .

according to Joule-Thomson principle :-

$$H = \text{Constant}$$

To write in differential form

$$dH = 0 \quad \text{--- (1)}$$

from the definition of enthalpy

$$H = U + PV$$

to write in differential form

$$dH = dU + d(PV)$$

$$\phi = \phi(x, y, z)$$

$$d\phi = \left(\frac{\partial \phi}{\partial x}\right) dx + \left(\frac{\partial \phi}{\partial y}\right) dy + \left(\frac{\partial \phi}{\partial z}\right) dz$$

$$dH = dU + PdV + VdP \quad \text{--- (2)}$$

From the first law of thermodynamics

$$dQ = dU + PdV \quad \text{--- (3)}$$

From the second law of thermodynamics

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

$$dQ = Tds \quad \text{--- (4)}$$

from eqn (3) and (4)

$$Tds = dU + PdV \quad \text{--- (5)}$$

from eq. (5) and (2)

$$dH = Tds + VdP$$

from eq (1)

$$0 = Tds + VdP$$

$$ds = -\frac{VdP}{T} \quad \text{--- (6)}$$

We know that, entropy is function of pressure and temperature. So that value of entropy in Joule - Thomson experiment depends upon pressure and temperature. So, in the form of function-

$$S = S(P, T)$$

To take total partial differential -

$$ds = \left(\frac{\partial s}{\partial p}\right)_T dp + \left(\frac{\partial s}{\partial T}\right)_p dT \quad \textcircled{7}$$

to put the value from eq. \textcircled{6}

$$\frac{-Vdp}{T} = \left(\frac{\partial s}{\partial p}\right)_T dp + \left(\frac{\partial s}{\partial T}\right)_p dT \quad \textcircled{8}$$

From the fourth equation of Maxwell

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad \textcircled{9}$$

by substituting value in eq. \textcircled{8} from eq. \textcircled{9}

$$\frac{-Vdp}{T} = -\left(\frac{\partial V}{\partial T}\right)_p dp + \left(\frac{\partial s}{\partial T}\right)_p dT$$

$$-Vdp = -T\left(\frac{\partial V}{\partial T}\right)_p dp + \left(T\frac{\partial s}{\partial T}\right)_p dT$$

from the second law of thermodynamics

$$dQ = T ds$$

then,

$$-Vdp = -T\left(\frac{\partial V}{\partial T}\right)_p dp + \left(\frac{\partial Q}{\partial T}\right)_p dT$$

$$-Vdp + T\left(\frac{\partial V}{\partial T}\right)_p dp = \left(\frac{\partial Q}{\partial T}\right)_p dT$$

$$\left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP = \left(\frac{\partial Q}{\partial T} \right)_P dT \quad \textcircled{10}$$

from the definition of heat capacity

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_P \quad (\text{Heat capacity at con. temperature})$$

put the value in eq. \textcircled{10}

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

H.T.C

$$M_H = \left(\frac{dT}{dP} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad \textcircled{11}$$

Equation \textcircled{11} is known as Joule-Thomson equation.

For those matter,

NOTE :- Joule-Thomson coefficient value find for those matter, only for those Joule-Thomson experiment works.

i.e. $M_H = 0$ (will not work)

$M_H \neq 0$ (will work)

**

Numerical :- Prove that Joule-Thomson experiment does not observe for ideal gas.

Solution:- We know that,

from ideal gas equation

$$P.V = R.T \quad \text{--- (1)}$$

Dif. with respect to T , $P = \text{Constant}$

$$P\left(\frac{\partial V}{\partial T}\right)_P = R \quad \text{--- (2)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad \text{--- (3)}$$

From eq. (1)

$$P.V = R.T$$

$$\frac{V}{T} = \frac{R}{P} \quad \text{--- (3)}$$

from eqn (2) and (3)

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

Again we know that,

from Joule-Thomson coefficient

$$u_H = \frac{1}{c_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad \text{--- (5)}$$

by substituting value from eq. (4)

$$u_H = \frac{1}{c_p} \left[T \cdot \frac{V}{T} - V \right]$$

$$\mu_H = 0 \quad \text{--- (6)}$$

hence, it is clear from eq. (6) that value of Joule - Thomson coefficient is zero for the ideal gas. therefore Joule - Thomson experiment does not observe for ideal gas.

Numerical

Prove that Joule - Thomson experiment observed for real gas.

Proof :-

We know that,

Equation for real gas
from van der waal equation

$$(P + \frac{a}{V^2})(V - b) = RT \quad \text{--- (1)}$$

where, a = Pressure constant

b = Volume constant

$$\frac{P + a}{V^2} = \frac{RT}{(V - b)}$$

D. with respect to T , $P = \text{Constant}$

$$0 + a \left(-\frac{2}{V^3} \right) \left(\frac{\partial V}{\partial T} \right)_P = R \left[1 \cdot \frac{1}{(V - b)} - T \cdot \frac{1}{(V - b)^2} \left(\frac{\partial V}{\partial T} \right)_P \right]$$

$$\Rightarrow \left[\frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right] \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{(V - b)}$$

$$\frac{RT}{(V-b)^2} \left[1 - \frac{2(V-b)^2\alpha}{RTV^3} \right] \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{(V-b)}$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = \frac{V-b}{\left[1 - \frac{2\alpha(V-b)^2}{RTV^3} \right]}$$

since $V \gg b$ { by neglecting high powers of b with respect to V }
then,

$$T \left(\frac{\partial V}{\partial T} \right)_P = \frac{V-b}{\left[1 - \frac{2\alpha V^2}{RTV^3} \right]}$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = \frac{V-b}{\left[1 - \frac{2\alpha}{RTV} \right]}$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = (V-b) \left[1 + \frac{2\alpha}{RTV} \right]^{-1}$$

from the Binomial theorem

$$(1+x)^{-n} = 1-nx$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = (V-b) \left[1 + \frac{2\alpha}{RTV} \right]$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = V-b + \frac{2\alpha V}{RTV} - \frac{2ab}{RTV}$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = V-b + \frac{2\alpha}{RT} - \frac{2ab}{RTV}$$

by neglect the term $\frac{2ab}{RTV}$

$$T \left(\frac{\partial V}{\partial T} \right)_P = V - b + \frac{2a}{RT} \quad \text{--- (2)}$$

Again we know that,
from the Joule-Thomson coefficient

$$\mu_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad \text{--- (3)}$$

by substituting value in eq. (3) from (2)

$$\mu_H = \frac{1}{C_P} \left[V - b + \frac{2a}{RT} - V \right]$$

$$\boxed{\mu_H = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right]} \quad \text{--- (4)}$$

It is clear from eq. (4) that Joule-Thomson coefficient is find for real gas. So Joule-Thomson experiment observed for Real gas.

Numerical (3) :- Prove that, $\left| \frac{E_S}{E_T} = \gamma \right|$

Where E = Elastic coefficient

E_T = Elastic coefficient for Isothermal system

E_S = Elastic coefficient for adiabatic system

$r =$ Ratio of heat capacity

$C_p =$ Heat capacity at constant pressure

$C_v =$ Heat capacity at constant volume

Proof :- From the definition of elastic coefficient

$$\text{Elastic coefficient} = \frac{\text{Stress}}{\text{strain}} \quad \textcircled{1}$$

from the definition of strain

$$\text{Strain} = \frac{-\text{change in volume}}{\text{Initial volume}} \quad \textcircled{2}$$

In the eq. ② -ve sign indicates decrease in volume.

Let initial volume of system is V and after applying stress dP change in volume of system becomes dV .

$$\text{then, Strain} = \frac{-dV}{V}$$

by substituting value in eq. ①

$$E = \frac{-dP}{dV/V}$$

$$E = -V \frac{dP}{dV}$$

To write partial differential form

$$E = -V \frac{\partial P}{\partial V}$$

(a) Elastic coefficient for isothermal system

$$E_T = -V \left(\frac{\partial P}{\partial V} \right)_T \quad \text{--- (3)}$$

(b) Now we know that, for the adiabatic system value of entropy remains constant. Therefore elastic coefficient

$$E_S = -V \left(\frac{\partial P}{\partial V} \right)_S \quad \text{--- (4)}$$

Now by dividing eq. (3) and (4)

$$\frac{E_S}{E_T} = \frac{-V \left(\frac{\partial P}{\partial V} \right)_S}{-V \left(\frac{\partial P}{\partial V} \right)_T}$$

$$\frac{E_S}{E_T} = \left(\frac{\partial P}{\partial V} \cdot \frac{\partial T}{\partial T} \right)_S$$

$$\frac{E_S}{E_T} = \left(\frac{\partial P}{\partial V} \cdot \frac{\partial S}{\partial S} \right)_T$$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial T}{\partial V} \right)_S}{\left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial S}{\partial V} \right)_T} \quad \text{--- (5)}$$

We know that,
from Maxwell's Relations.

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

$$2. \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$3. \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

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

On putting values in eq. ⑤ from Maxwell's equation.

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

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

$$\underline{E_S} = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial V}\right)_P$$

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

$$\underline{E_S} = \left(\frac{\partial V}{\partial T} \cdot \frac{\partial S}{\partial V}\right)_P$$

$$\underline{E_T} = \left(\frac{\partial P}{\partial T} \cdot \frac{\partial S}{\partial P}\right)_V$$

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

$$\frac{E_S}{E_T} = \frac{T \left(\frac{\partial S}{\partial T} \right)_P}{T \left(\frac{\partial S}{\partial T} \right)_V} = \frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial S}{\partial T} \right)_V} \quad \textcircled{6}$$

From the second law of thermodynamics

$$\delta Q = T \delta S \quad (\text{Partial form})$$

by putting value in eq. ⑥

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial Q}{\partial T} \right)_P}{\left(\frac{\partial Q}{\partial T} \right)_V} \quad \textcircled{7}$$

From the definition of heat capacity

$$C = \left(\frac{\partial Q}{\partial T} \right)$$

by substituting value in eq. ⑦

$$\frac{E_S}{E_T} = \frac{C_P}{C_V} \quad \textcircled{8}$$

We know that, ratio of heat capacity

$$\gamma = \frac{C_P}{C_V} \quad \textcircled{9}$$

from eq. ⑧ and ⑨

$$\frac{E_S}{E_T} = \gamma$$

- Heat Engine :- The engine which converts heat energy into mechanical energy (work energy) is called Heat engine.

In the heat engine such type of matters are used that they pass from different-different states and again come into initial state. i.e change in internal energy (ΔU) of matter is zero. ($\Delta U=0$) This matter is called working substance.

There are three parts of Heat-Engine -

1. Heat Source
2. Heat Sink
3. Working matter and mechanical arrangement

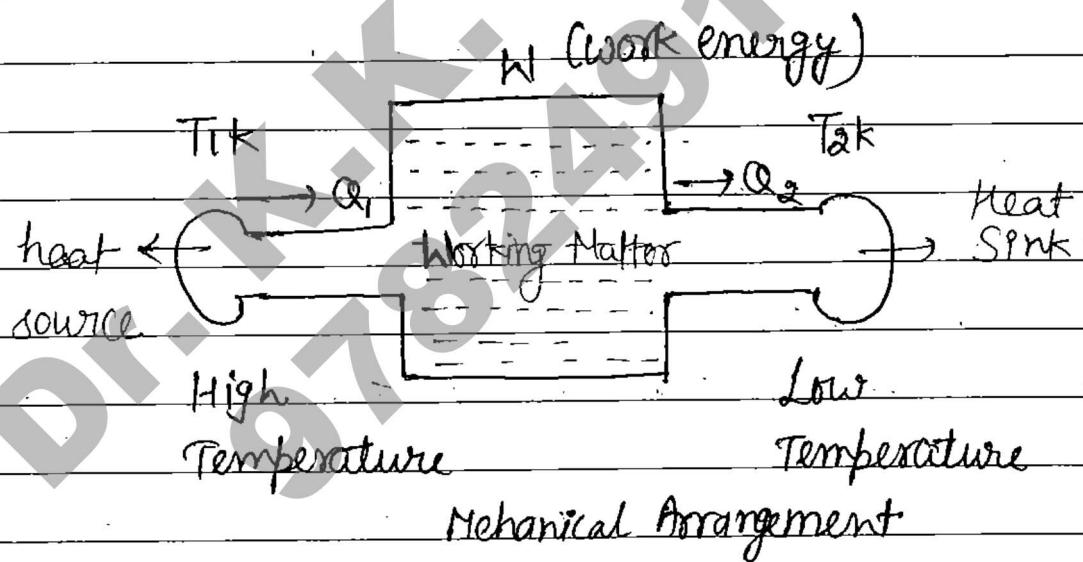
1. Heat Source :- Heat source is a store of heat. Heat capacity of heat source is infinite and temperature of heat source is high. Let the temperature of heat source is $T_1 K$

2. Heat Sink :- Heat sink is also a store of heat. which have infinite heat capacity.

But it is cold store which has minimum temperature. Suppose temperature of heat sink is T_{A} .

3. Working Matter and Mechanical Arrangement :-

In the heat engine such type of matter are used that they pass from different state and again come back into initial stage. It means, change in internal energy dU of matter is zero. ($dU=0$) This matter is called working substance.



- Efficiency of Heat Engine :- Efficiency of heat of heat engine is represented by η

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

where, Q_1 = Heat taken from heat source
 Q_2 = Heat given to the heat sink
 η = Efficiency of heat engine

Proof :- Efficiency :- Ratio of Work and heat taken from heat source is said to be efficiency of heat engine.

$$\text{Efficiency of heat engine} = \frac{\text{Work}}{\text{Heat of heat source}}$$

$$\eta = \frac{W}{Q_1} \quad \textcircled{1}$$

From, the first law of thermodynamics

$$dQ = dU + dW$$

from property of working-matter ($dU=0$)
by put the value

$$dQ = dW \quad \textcircled{2}$$

so, change in heat

$$dQ = Q_2 - Q_1$$

so, work done is

$$dW = -W \quad (\text{By system})$$

by put the value in eq. $\textcircled{2}$

$$Q_2 - Q_1 = -W$$

$$Q_1 - Q_2 = W$$

by substituting value in eq. ①

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

$$\boxed{\eta = 1 - \frac{Q_2}{Q_1}} \quad \text{--- } ③$$

Eqn ③ is called expression of efficiency of heat engine.

* • Carnot Engine :- Scientist Carnot imagine a theoretical heat engine. this heat engine is known as Carnot Engine.

According to Carnot efficiency of this heat engine is 100% which is impossible.

There are four main parts of Carnot Engine -

1. Heat source
2. Heat sink
3. Working matter and mechanical arrangement
4. Stand

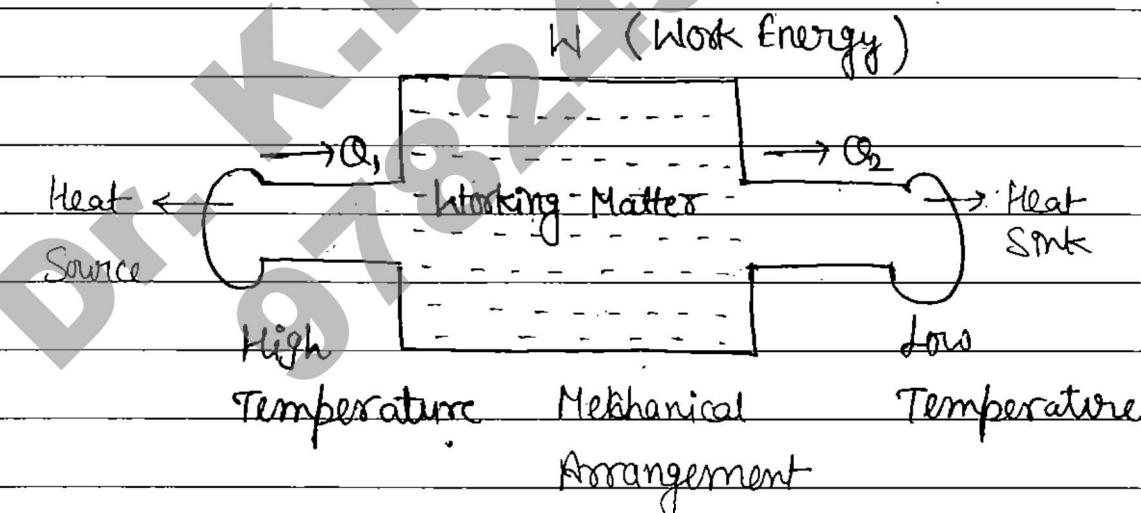
1. Heat Source :- Heat source is a source of heat. Heat capacity of heat source is infinite and temperature is in high let the temperature of heat source is T_1 , K. upper surface is perfectly conducting

2. Heat Sink :- Heat sink is also a store of heat which has infinite heat capacity. But it is a cold store, which has minimum temperature. Suppose, temperature of heat sink is $T_{\text{A,k}}$.

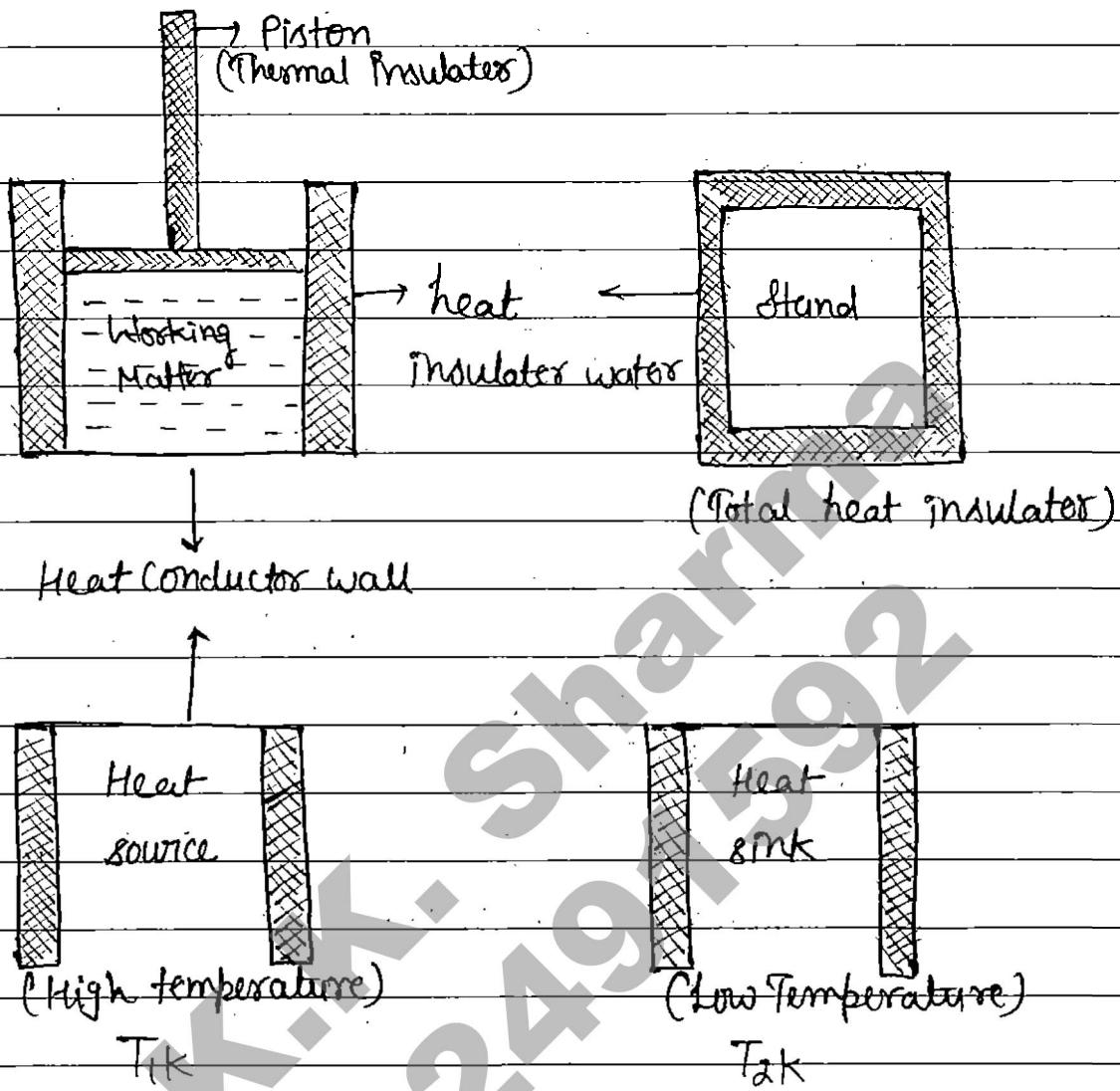
3. Working Matter and Mechanical Arrangement :-

In the heat engine such type of matter is used that they can come back to the initial stage after passing from different-different states. It means, change in internal energy dU of matter is zero ($dU = 0$). This matter is called working matter.

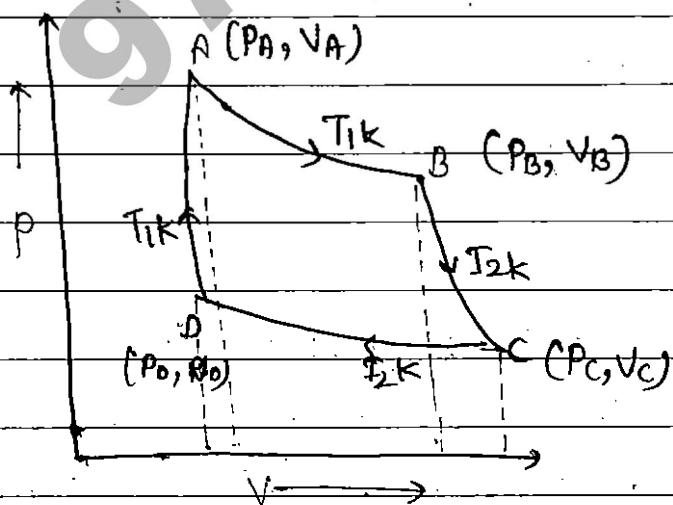
*Working
matter*



4. Stand :- It is a thermal insulator system. Due to which exchange of heat does not take place. It means, this system represents an adiabatic process.



Carnot Engine is explained by four process.



(Q) First Process (Isothermal expansion) :- First of all we put working matter on heat source. Due to which temperature of working matter becomes T_1 , K. This point is denoted by A in the curve. At this instant, pressure of working matter is P_A and volume is V_A .

Now we, pull the piston upwards due to which volume becomes V_B from V_A and pressure becomes P_B and from P_A . In the curve, this part is denoted by AB. Therefore, internal energy of working matter decreases. Due to which, temperature of working matter also decrease ($U = kT$).

The temperature decrease of working matter same quantity of temperature is taken from heat source, due to which temperature of working matter remains constant. (T_1 , K). Therefore this process is called isothermal process.

We know that,

$$W = \int_{V_A}^{V_B} P dV$$

From ideal gas equation

$$PV = RT_1 \quad (\text{for AB part of curve})$$

$$P = \frac{RT_1}{V}$$

on putting value

$$W_1 = \int_{V_A}^{V_B} \frac{RT_1}{V} dV$$

$$W_1 = RT_1 \int_{V_A}^{V_B} \frac{1}{V} dV$$

$$W_1 = RT_1 \left[\log_e V \right]_{V_A}^{V_B}$$

$$W_1 = RT_1 \log_e \frac{V_B}{V_A}$$

$$\text{Q}_1 = W_1 = 2.303 RT_1 \log_e \frac{V_B}{V_A} \quad \textcircled{1}$$

(b) Second Process (Adiabatic Expansion)

Now, we put the working matter on the stand. Stand is totally heat insulator. That's why it do not exchange the heat. It means, this process will be adiabatic.

Now, we pull the piston upwards due to which volume increases and becomes V_B to V_c and pressure becomes P_B to P_c but there is a decrease in pressure. Therefore, temperature of working matter

$$T V^{r-1} = k \text{ (for } T_2 V)$$

decreases and becomes $T_2 k$ from $T_1 k$. In the curve, this process is denoted by BC.

Mathematical Analysis

We know that,

$$W_2 = \int_{V_B}^{V_C} P dV$$

From adiabatic state equation

$$P V^r = k$$

$$P = k V^{-r}$$

$$\text{Here } r = \frac{C_p}{C_v}$$

on putting value

$$W_2 = \int_{V_B}^{V_C} k V^{-r} dV$$

$$W_2 = k \left[\frac{V^{-r+1}}{-r+1} \right]_{V_B}^{V_C}$$

$$W_2 = \frac{k V_C^{1-r} - k V_B^{1-r}}{1-r} \quad \text{--- (2)}$$

From ideal gas equation

$$P_B V_B = R T_1 \quad (\text{for point B}) \quad \text{--- (3)}$$

$$P_C V_C = R T_2 \quad (\text{for point C}) \quad \text{--- (4)}$$

From adiabatic state equation

$$PV^r = K$$

$$P_B = KV_B^{-r} \quad \text{--- (c) (for point B)}$$

$$P_C = KV_C^{-r} \quad \text{--- (d) (for point C)}$$

From eq.n (a) and (c)

$$KV_B^{-r} V_B = RT_1$$

$$KV_B^{1-r} = RT_1 \quad \text{--- (e)}$$

From eq.n (b) and (d)

$$KV_C^{1-r} = RT_2 \quad \text{--- (f)}$$

by substituting values in eq. (g) from eq. (e) & (f)

$$W_2 = \frac{RT_2 - RT_1}{1-r}$$

$$\boxed{W_2 = -R(T_1 - T_2)} \quad \therefore \quad \text{(g)}$$

(c) Third Process (Isothermal Compression) -

Now we put the working matter on the heat sink. In this state temperature of working matter is T_{ak} . We know that heat sink is store of heat and this is a heat conductor due to which exchange of heat

takes place.

Now we move piston downwards due to which volume decreases and becomes V_0 to V_c and pressure increases and becomes P_0 from P_c . Due to which temperature of working matter increases. The temperature which is increasing same quantity of heat is given to heat sink due to which temperature remains constant of working matter. Therefore this process is called isothermal compression.

We know that,

$$W_3 = \int_{V_c}^{V_0} P dV$$

From ideal gas equation

$$PV = RT_2$$

(for CD part of curve)

$$P = \frac{RT_2}{V}$$

On putting values

$$W_3 = \int_{V_c}^{V_0} \frac{RT_2}{V} dV$$

$$W_3 = RT_2 \left[\log_e V \right]_{V_c}^{V_0}$$

$$W_3 = RT_2 \log_e \frac{V_0}{V_c}$$

$$W_3 = 2.303 RT_2 \log_{10} \frac{V_0}{V_c} \quad \text{--- (4)}$$

(d) Fourth Process (Adiabatic Compression) :-

Now, we put the working matter on the stand. At this time temperature of working matter is T_2 K.

Again, piston is moved to downwards due to which volume decreases from V_0 to V_A . and pressure increases from P_0 to P_A . Therefore temperature of working matter increases from T_2 K to T_1 K. Because, stand does not exchange the heat it means process is called adiabatic compression process. In the curve, this process is denoted by DA.

This cycle is known as Carnot cycle.

Mathematical Analysis

We know that,

$$W_4 = \int_{V_0}^{V_A} P dV$$

From adiabatic state equation

$$PV^r = k$$

$$P = KV^{-r}$$

on putting value

$$W_4 = \int_{V_B}^{V_A} KV^{-r} dV$$

$$W_4 = K \left[\frac{V^{-r+1}}{-r+1} \right]_{V_B}^{V_A}$$

$$W_4 = \frac{KV_A^{1-r} - KV_B^{1-r}}{1-r}$$

$$\therefore KV_A^{1-r} = RT_1$$

$$\therefore KV_B^{1-r} = RT_2$$

by substituting values

$$W_4 = \frac{R(T_1 - T_2)}{1-r} \quad \text{--- (5)}$$

(e) Resultant work

hence, the resultant work done by Carnot's engine

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

by substituting values from eq. n (1), (3), (4) & (5)

$$W = 2.303 RT_1 \log_{10} \frac{V_B}{V_A} - \frac{R(T_1 - T_2)}{1-r} + 2.303 RT_2 \log_{10} \frac{V_B}{V_C} + \frac{R(T_1 - T_2)}{1-r}$$

$$W = 2.303 RT_1 \log_{10} \frac{V_B}{V_A} - 2.303 RT_2 \log_{10} \frac{V_C}{V_B} \quad \text{--- (6)}$$

Now from adiabatic state equation.

$$T_1 V_A^{\gamma-1} = K \quad \text{--- (A) (for point A in curve)}$$

$$T_1 V_B^{\gamma-1} = K \quad \text{--- (B) (for point B)}$$

$$T_2 V_C^{\gamma-1} = K \quad \text{--- (C) (for point C)}$$

$$T_2 V_D^{\gamma-1} = K \quad \text{--- (D) (for point D)}$$

For adiabatic process

- (i) For BC part of curve —
from eq. (B) and (C)

$$T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left(\frac{V_C}{V_B} \right)^{\gamma-1} \quad \text{--- (E)}$$

- (ii) For DA part of curve —

from eq. (D) and (A)

$$T_1 V_A^{\gamma-1} = T_2 V_D^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left(\frac{V_D}{V_A} \right)^{\gamma-1} \quad \text{--- (F)}$$

$$\boxed{\left(\frac{T_1}{T_2} \right)^{1/\gamma-1} = \frac{V_D}{V_A} = \rho} \quad (\text{Adiabatic expansion coefficient})$$

From eq. (E) and (F)

$$\left(\frac{V_C}{V_B}\right)^{r-1} = \left(\frac{V_B}{V_A}\right)^{r-1}$$

$$\frac{V_C}{V_B} = \frac{V_B}{V_A}$$

$\frac{V_C}{V_B} = \frac{V_B}{V_A}$	—————	(6)
$\frac{V_C}{V_B} = \frac{V_B}{V_A}$		

By putting value in eq. (6)

$$W = 2.303 RT_1 \log_{10} \left(\frac{V_B}{V_A} \right) = 2.303 RT_2 \log_{10} \left(\frac{V_B}{V_A} \right)$$

$$W = 2.303 R (T_1 - T_2) \log_{10} \left(\frac{V_B}{V_A} \right) \quad \text{--- (7)}$$

(f) Efficiency of Carnot's Engine -

since, we know that

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

by putting values from eq. (1) and (7)

$$\eta = \frac{2.303 R (T_1 - T_2) \log_{10} \left(\frac{V_B}{V_A} \right)}{2.303 RT_1 \log_{10} \left(\frac{V_B}{V_A} \right)}$$

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

M.T.P.

$$\boxed{\eta = 1 - \frac{T_2}{T_1}} \quad \text{--- } ⑧$$

Equation ⑧ is called formula for efficiency of Carnot engine.

$$\because \left(\frac{T_1}{T_2}\right)^{r-1} = p \quad (\text{Adiabatic expansion ratio})$$

$$\frac{T_1}{T_2} = (p)^{r-1}$$

$$\frac{T_2}{T_1} = \left(\frac{1}{p}\right)^{r-1}$$

by putting value in eq. ⑧

$$** \quad \boxed{\eta = 1 - \left(\frac{1}{p}\right)^{r-1}} \quad ⑨$$

⑧ Special Points -

- (i) It is clear from eq. ⑧ that efficiency of Carnot Engine (η) does not depend upon ~~the~~ nature of working substance.
- (ii) The efficiency of Carnot engine (η) depends upon temperature of heat source (T_1 , K) and temperature of heat sink (T_2 , K).
- (iii) If $T_2 = 0\text{K}$ and $T_1 = \infty\text{K}$, then efficiency

of Carnot engine will be 100% which is imagination of Carnot engine. This condition is impossible. Therefore, conceive of Carnot engine is theoretical.

- (N) It is clear from eq. (9) that efficiency of Carnot engine depends upon adiabatic expansion coefficient (γ).

Important Numerical

Given: $T_2 = 27^\circ\text{C} = 300\text{K}$

$$T_1 = 327^\circ\text{C} = 600\text{K}$$

$$\eta = ?$$

Solution We know that,

Efficiency of Carnot engine

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

On putting values

$$\eta = 1 - \frac{600}{300}$$

$$\eta = 1 - \frac{1}{2} = \frac{1}{2} \times 100\%$$

$$\boxed{\eta = 50\%}$$

2:

Given $T_2 = 0^\circ\text{C} = 273\text{K}$ then $\eta = ?$

$$T_1 = 100^\circ\text{C} = 373\text{K}$$

Solution

We know that,

$$\text{Efficiency of Carnot Engine } \eta = 1 - \frac{T_2}{T_1}$$

$$\text{then, } \eta = 1 - \frac{273}{373}$$

$$\eta = \frac{100}{373} \times 100\%$$

$$\boxed{\eta = 26.03\%}$$

Note:-

Efficiency of Carnot Engine -

$$\eta_c = 1 - \frac{T_2}{T_1} \quad \text{①}$$

Efficiency of Heat Engine

$$\eta_H = 1 - \frac{Q_2}{Q_1} \quad \text{②}$$

by comparing eq. ① and ②

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

3.

Given : $W = 100 \text{ kW} = 10^5 \text{ W}$

$$T_1 = 490 \text{ K}, T_2 = 290 \text{ K}$$

Calculate : ③ Absorbed heat $Q_1 = ?$

$$\textcircled{b} \quad Q_2 = ?$$

$$\textcircled{c} \quad \eta = ?$$

Solution

We know that,

(P) Amount of heat absorbed $Q_1 = \frac{W T_1}{T_1 - T_2}$

$$Q_1 = \frac{10^5 \times 490}{490 - 290} = 2.45 \times 10^5 \text{ W}$$

$$= 245 \text{ kW}$$

(ii) Amount of heat rejected $Q_2 = Q_1 - W$

$$\Rightarrow 245 - 100$$

$$= 145 \text{ kW}$$

(iii) Efficiency $\eta = 1 - \frac{T_2}{T_1} \Rightarrow 1 - \frac{290}{490} \times 100\%$

$$= 0.408 \times 100\%$$

$$= 40.8\%$$

Given $W = 1 \text{ kW} = 10^3 \text{ W}$

$T_1 = 327^\circ\text{C} = 600\text{K}$

$T_2 = 27^\circ\text{C} = 300\text{K}$

Calculate : (a) $Q_1 = ?$ (b) $Q_2 = ?$ (c) $\eta = ?$

Solution (a) $\because \eta = \frac{W}{Q_1} \quad \text{--- (1)}$ and $\eta = 1 - \frac{T_2}{T_1} \quad \text{--- (2)}$

From eq. (1) and (2)

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

$$= \frac{1000 \times 600}{(600 - 300)} = 2000 \text{ kW}$$

(b) $Q_2 = Q_1 - W$
 $= 2000 - 1000 = 1000 \text{ kJ}$

(c) Efficiency $\eta = \frac{T_1 - T_2}{T_1}$
 $= \frac{600 - 300}{600} = 0.5$
 $= 50\%$

5. Given: ~~Q1~~ $T_2 = 0^\circ\text{C}$, $\eta = 68\% = 0.68$
 $T_1 = ?$

Solution: $T_2 = 273 \text{ K}$

since, we know that

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

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

$$T_1 = \frac{273}{1 - 0.68} = \frac{273}{0.32}$$

$$T_1 = 853.1 \text{ K}$$

Given: $Q_1 = 1000$, $Q_2 = 400$
 $T_1 = 200$, $T_2 = ?$, $\eta = ?$

Solution :- since, we know that

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

$$T_2 = \frac{400}{1000} \times 500 = 200\text{K}$$

$$\text{Q: } \eta = 1 - \frac{T_2}{T_1} \Rightarrow 1 - \frac{200}{200}$$

$$\eta = 60\%$$

Q: Given: $\eta = 66\%$, $r = 1.5$, $P = ?$

Solution: We know that,

Efficiency of Carnot engine -

$$\eta = \left[1 - \left(\frac{1}{P} \right)^{r-1} \right]$$

$$\left(\frac{1}{P} \right)^{r-1} = 1 - \eta$$

$$P = \left(\frac{1}{1-\eta} \right)^{1/(r-1)}$$

$$P = \left(\frac{1}{1-0.66} \right)^{1/(1.5-1)}$$

$$P = \left(\frac{1}{0.34} \right)^2 = \left(\frac{100}{34} \right)^2$$

$$P = 8.65$$

Q: Given $r = 1.5$, $P = 4$, $\eta = ?$

Solution: The efficiency of Carnot engine

$$\eta = \left[1 - \left(\frac{1}{P} \right)^{r-1} \right]$$

$$\eta = \left[1 - \left(\frac{1}{4} \right)^{1.5-1} \right]$$

$$\eta = 1 - \left(\frac{1}{4} \right)^{1/2}$$

$$\eta = 0.5 \Rightarrow \boxed{\eta = 50\%}$$

9: Given : $T_1 = 227^\circ C = 500K$

$$T_2 = 27^\circ C = 300K$$

$$r = 1.5, p = ?, \eta = ?$$

Solution: (a) We know that

$$p = \left(\frac{T_1}{T_2} \right)^{1/r-1}$$

$$= \left(\frac{500}{300} \right)^{1/1.5-1} = \left(\frac{5}{3} \right)^{1/0.5}$$

$$p = \left(\frac{5}{3} \right)^2 = 2.79$$

(b) Efficiency $\eta = 1 - \frac{T_2}{T_1}$

$$\eta = 1 - \frac{300}{500} = \frac{2}{5}$$

$$\eta = 0.4 \times 100\%$$

$$\boxed{\eta = 40\%}$$

10: Given : $T_1 = 600K$

$$T_2 = 300K$$

$$\eta = 52\%$$

Solution: We know that

Efficiency of Carnot Engine

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

$$\eta_c = 1 - \frac{300}{600} = \frac{1}{2} 100\%.$$

$$\eta_c = 50\%.$$

hence, efficiency of Carnot engine occurs 50%.

There is no any engine which have more efficiency than Carnot engine.

* * * * *

Efficiency of Carnot Engine is 40% and efficiency becomes 20% more after decreasing 100% in temperature of sink. Then, calculate the temperature of sink T_2 .

Solution:- We know that,

$$\text{Efficiency of Carnot Engine } \eta = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{T_2}{T_1} = (1-\eta)$$

$$\Rightarrow T_2 = (1-\eta)T_1 \quad \text{--- (1)}$$

$$\therefore \eta = 40\% = 0.4$$

$$T_2 = (1-0.4)T_1 = 0.6T_1 \quad \text{--- (2)}$$

According to question
from eq. (1)

$$T_2 - 100 = (1-0.6)T_1 = 0.4T_1 \quad \text{--- (3)}$$

Now eq. (3) / eq. (2)

$$\frac{T_2 - 100}{T_2} = \frac{0.4T_1}{0.6T_1} = \frac{2}{3}$$

$$T_2 - 100 = \frac{2}{3}T_2$$

$$T_2 - \frac{2}{3}T_2 = 100$$

$$\frac{T_2}{3} = 100 \Rightarrow T_2 = 300^\circ\text{C}$$

12.

Given: for 1st Carnot Engine -

$$T_1 = 750\text{K}, T_2 = 375\text{K}, \eta_I = ?$$

For second Carnot Engine

$$T_1 = 2\text{K}, T_2 = 500\text{K}, \eta_{II} = ?$$

$$[\eta_I = \eta_{II}]$$

Solution: We know that

Efficiency of Carnot engine

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

for 1st Carnot engine -

$$\eta_I = 1 - \frac{375}{750} = \frac{375}{750} = \frac{1}{2} \times 100\% = 50\%$$

$$[\eta_I = 50\%]$$

since, $\eta_I = \eta_{II}$

$$\text{so, } \eta_{II} = 50\%$$

for the second Carnot engine

$$\eta_{II} = 1 - \frac{T_2}{T_1}$$

$$\eta_{II} = 1 - \frac{500}{T_1} \Rightarrow \frac{500}{T_1} = 1 - \eta_{II}$$

$$T_1 = \frac{500}{1 - \eta_{II}} = \frac{500}{1/2} = 1000$$

$$\boxed{T_1 = 1000\text{K}}$$

- Q13: Efficiency of a Carnot engine is 50% and after decreasing 100°C in T_2 (sink) efficiency becomes 70%.

Solution:- We know that

Efficiency of Carnot engine -

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

$$\frac{T_2}{T_1} = 1 - \eta \Rightarrow T_2 = (1 - \eta)T_1 \quad \text{--- } ①$$

$$\therefore \eta = 50\% = 0.5$$

$$T_2 = (1 - 0.5)T_1 \Rightarrow T_2 = 0.5T_1 \quad \text{--- } ②$$

According to the question

$$T_2 - 100 = (1 - 0.7)T_1$$

$$T_2 - 100 = 0.3T_1 \quad \text{--- } ③$$

from eq. ② and ③

$$T_2 - T_2 + 100 = 0.5T_1 - 0.3T_1$$

$$100 = 0.2T_1$$

$$\therefore T_1 = \frac{100}{0.2} = 500$$

$$\Rightarrow [T_1 = 500^\circ\text{C}]$$

14. Efficiency of a Carnot engine is 50% and temperature of sink is 7°C what should be the increase in temp. of source that the efficiency becomes 70%.

Solution :- Given: $n = 50\% = 0.5$

$$T_2 = 7^\circ\text{C} = 280\text{K}$$

$$T_2 = (1-n)T_1 \Rightarrow T_1 = \frac{T_2}{(1-n)}$$

$$T_1 = \frac{280}{(1-0.5)}$$

$$T_1 = \frac{280}{0.5} = 560\text{K}$$

According to the question,

$$T'_1 = \frac{280}{(1-0.7)} = \frac{280}{0.3} \quad \therefore n = 0.7 = 70\%$$

$$T'_1 = 933\text{K}$$

change in source temperature

$$\Delta T = T'_1 - T_1 \Rightarrow 933 - 560 = 373\text{K}$$

- Thermodynamic Scale of Temperature

This thermodynamic scale of temperature was manufactured by scientist Kelvin. Generally, thermometers have dependence upon nature of working matter.

"The scale temperature which works on Carnot engine principle, is called thermodynamic scale of temperature." We know that Carnot engine does not depend upon the nature of working matter, it depends only upon initial temperature (T_1) and final temperature (T_2). Similarly, thermodynamic scale of temperature also depends upon initial temperature and final temperature. So, it does not depend upon mid state.

Mathematical Analysis - In order to mathematical analysis of thermodynamics scale of temperature we imagine a heat engine. Suppose this heat engine works between temperature Q_1 and Q_2 . At the Q_1 temperature, Q_1 heat is accepted from heat source and Q_2 heat is released to heat sink at the temperature Q_2 . So, efficiency of heat engine -

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

$$(Q_1 > Q_2 ; Q_1 > Q_2)$$

according to Carnot, efficiency of Carnot engine depends upon temperature θ_1 and θ_2 .

it means, efficiency of Carnot engine is function of temperature θ_1 and θ_2 .

So, in the form of function

$$\eta = f(\theta_1, \theta_2) \quad \text{--- (2)}$$

Now from eq. (1)

$$\eta = 1 - \frac{\theta_2}{\theta_1}$$

$$\frac{\theta_2}{\theta_1} = 1 - \eta$$

$$\frac{\theta_1}{\theta_2} = \frac{1}{1-\eta}$$

on putting value from eq. (2)

$$\left| \begin{array}{l} \frac{\theta_1}{\theta_2} = \frac{1}{1-f(\theta_1, \theta_2)} \\ \qquad \qquad \qquad = F(\theta_1, \theta_2) \end{array} \right| \text{ New function} \quad \text{--- (3)}$$

New function $F(\theta_1, \theta_2)$ also depend upon temp. θ_1 and θ_2 .

If Carnot engine works between temperature θ_2 and θ_3 then, at the temperature θ_2 , if θ_2 heat accepted by heat source and θ_3 heat is released to heat sink at temperature θ_3 .

So, from eq. ③

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3) \quad \text{--- } ④$$

$$(\theta_2 > \theta_3 ; Q_2 > Q_3)$$

If Carnot engine works between temperature θ_1 and θ_3 then at the temperature θ_1 , Q_1 heat is accepted from heat source and Q_3 heat is released to heat sink at the temperature θ_3 .

from eq. ③

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_3) \quad \text{--- } ⑤$$

$$(\theta_1 > \theta_3 , Q_1 > Q_3)$$

$$\text{Now } \frac{\theta_1}{\theta_3} = \frac{Q_1}{Q_3} \cdot \frac{Q_2}{Q_1}$$

$$\frac{\theta_1}{\theta_3} = \frac{Q_1}{Q_2} \cdot \frac{Q_2}{Q_3}$$

by substituting values from eq. ③, ④ and ⑤

$$F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \cdot F(\theta_2, \theta_3) \quad \text{--- } ⑥$$

In the R.H.S of equation ⑥ mid state of temp. θ_2 is find which contradicts principle of Carnot-engineer. Because Carnot engine only depends upon initial and final temperature. So, dependency of θ_2 have to be shift from eq. ⑥

Now we solve eqn ⑥ by mathematical method, from variable separation method,

Let function $F(\theta_1, \theta_2)$ is present in following form.

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)} \quad \text{--- } ⑦$$

Similarly,

$$F(\theta_2, \theta_3) = \frac{\phi(\theta_2)}{\phi(\theta_3)} \quad \text{--- } ⑧$$

$$F(\theta_1, \theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_3)} \quad \text{--- } ⑨$$

by substituting value in eq. ⑥ from ⑦, ⑧ ⑨

$$\frac{\phi(\theta_1)}{\phi(\theta_3)} = \frac{\phi(\theta_1)}{\phi(\theta_2)} \cdot \frac{\phi(\theta_2)}{\phi(\theta_3)}$$

$$\frac{\phi(\theta_1)}{\phi(\theta_3)} = \frac{\phi(\theta_1)}{\phi(\theta_3)} \quad \text{--- } ⑩$$

hence, it is clear from eq. ⑩ that Carnot engine depends upon temperature θ_1 and θ_3 . So, does not depend upon mid state (θ_2).

from eqn ③ and ⑦

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

$$\frac{\theta_2}{\theta_1} = \frac{\phi(\theta_2)}{\phi(\theta_1)} \quad \text{--- } ⑪$$

on putting value in eq. ① from ⑪

$$\eta = 1 - \frac{\phi(O_2)}{\phi(O_1)}$$

Let $\phi(O_1) = T_1$ {New Function}
 $\phi(O_2) = T_2$

by putting value.

~~ATC~~

$\eta = 1 - \frac{T_2}{T_1}$	— ⑫
------------------------------	-----

efficiency of

It is clear from eq. ⑫ thermodynamic scale of temperature depends upon initial temperature T_1 and final temperature T_2 .

We know that,

Efficiency of ideal Carnot Engine (Ideal thermometer) is following -

$$\eta = 1 - \frac{T_2}{T_1} \quad — ⑬$$

by comparing eq. ⑪ and ⑬

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

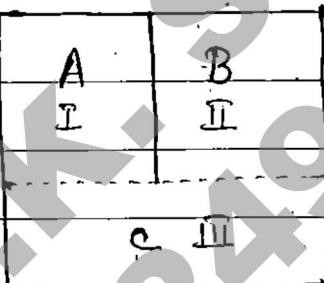
$\frac{T_2}{T_1} = \frac{T_2}{T_1}$	— ⑭
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It is clear from eq. ⑭ that thermodynamic scale

Temperature and ideal thermometer both are equivalent to each other.

- Zeroth Law of Thermodynamics :-

Zeroth law of thermodynamic defines temperature. According to zeroth law of thermodynamic "If two systems are in thermal equilibrium condition with a other system then, they will be in thermal equilibrium condition with each other."

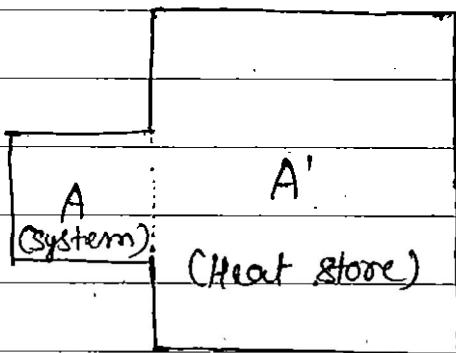


Suppose there are ^{three} two systems A and B, C.

Two systems A and B are in thermal-equilibrium condition with system - C. Then system A and B also in thermal-equilibrium condition to each other, this zeroth law of thermodynamics.

Common physical quantity in all the three system is said to be temperature in thermodynamic physics.

- System in Contact with Heat Store :-



Let there are two system A and A'. System - A' is a heat store. We know that, heat capacity of heat store is infinite. When system - A and heat store A' are kept in contact to each other then exchange of heat takes place. But there is no change occurs in temperature of heat store. It means, remains unchanged.

Due to exchange of heat a combined system A^* is formed. Suppose, energy of this combined system is E^* and energy of heat store A' is E' and energy of system - A is E . Let energy of ith particle present in system - A is E_i . According to energy conservation law -

$$E^* = E' + E$$

$$E' = E^* - E \quad \text{--- (1)}$$

Note $E^* = E' + E$

$$\because E' \gg E$$

$$E^* = E' \quad \text{--- (2)}$$

Mathematical Analysis :-

Accessible State :- The micro state which follows law of system, is said to be accessible state.

Accessible state depends upon energy it means it present in the form of energy function. It is denoted by $\Omega(E)$.

Let accessible state of the system - A is $\Omega(E)$ and accessible state of system A' is $\Omega'(E')$ and $\Omega^*(E^*)$ is accessible state of combined system A*.

From the definition of probability

$$P(E) \propto \Omega'(E')$$

$$P(E) = C \Omega'(E')$$

by putting value from eq. ①

$$[P(E) = C \Omega^*(E^* - E)] \quad \text{--- } ③$$

Where, C = Proportional Constant

$P(E)$ = Probability of system - A

$\Omega'(E')$ = Accessible state of system - A'
(Heat store)

Value of $\Omega'(E^* - E)$ present in eq. ③ is calculated by mathematical method Taylor expansion.

Now from the Taylor

$$\log n'(E^*-E) = \log n'(E^*) - \left[\frac{\partial \log n'(E^*)}{\partial E'} \right] E + \frac{1}{2} \left[\frac{\partial^2 \log n'(E^*)}{\partial E'^2} \right] E^2 + \dots$$

$$\because E' \gg E$$

by neglecting terms of high powers of E'

$$\log n'(E^*-E) = \log n'(E^*) - \left[\frac{\partial \log n'(E^*)}{\partial E'} \right] E$$

$$\text{Let } \beta = \frac{1}{kT} = \frac{\partial \log n'(E^*)}{\partial E'}$$

on putting value,

$$\log n'(E^*-E) = \log n'(E^*) - \beta E$$

$$\log \left[\frac{n'(E^*-E)}{n'(E^*)} \right] = -\beta E$$

by taking antilog

$$\frac{n'(E^*-E)}{n'(E^*)} = e^{-\beta E} \quad (\text{Boltzmann factor})$$

$$\boxed{n'(E^*-E) = n'(E^*) e^{-\beta E}} \quad \text{--- (4)}$$

by put the value in eq.③ from eq.④

$$P(E) = C \Omega'(E^*) e^{-\beta E}$$

$\therefore C' = C \Omega'(E^*)$ (New Constant)

$$P(E) = C' e^{-\beta E} \quad \text{--- (5)}$$

Equation (5) defines probability. value of constant C' present in eq. (5) can be find by the help of property of probability.

Probability of i^{th} partical

$$P(E_i) = C' e^{-\beta E_i} \quad \text{--- (6)}$$

for the whole system-

$$\sum_{i=1}^n P(E_i) = \sum_{i=1}^n C' e^{-\beta E_i}$$

$$\sum_{i=1}^n P(E_i) = C' \sum_{i=1}^n e^{-\beta E_i} \quad \text{--- (7)}$$

By the definition of normalisation relation

$$\sum_{i=1}^n P(E_i) = 1$$

on putting value in eq. (7)

$$1 = C' \sum_{i=1}^n e^{-\beta E_i}$$

$$C' = \frac{1}{\sum_{i=1}^n e^{-\beta E_i}}$$

by substituting value in eq.⑦

~~BY THE~~

$$P(E_i) = \frac{e^{-\beta E_i}}{\sum_{i=1}^n e^{-\beta E_i}} \quad \text{--- } ⑧$$

Equation ⑧ is called probability distribution function. or canonical function.

Partition Function :- Addition of all the accessible state is called partition function of system. Partition function is denoted by Z.

So, the partition function of system

$$Z = \sum_{i=1}^n e^{-\beta E_i}$$

on putting value in eq.⑧

~~BY THE~~

$$P(E_i) = \frac{e^{-\beta E_i}}{Z} \quad \text{--- } ⑨$$

Equation ⑨ denotes probability in the form of partition function.

- Application of Probability distribution Function

1. Mean Energy of System — By the help of probability function, average of physical quantity can be find.

Example: — Let Y is a physical quantity.
So, average of Y

$$\bar{Y} = \sum_{i=1}^n Y_i P(E_i)$$

so, average of internal energy of system

$$\bar{E} = \sum_{i=1}^n E_i P(E_i) \quad \text{--- (i)}$$

from eq. (3), $P(E_i) = \frac{e^{-\beta E_i}}{Z}$

On putting value in eq. (i)

$$\bar{E} = \frac{\sum_{i=1}^n E_i e^{-\beta E_i}}{Z} \quad \text{--- (ii)}$$

$$\therefore Z = \sum_{i=1}^n e^{-\beta E_i}$$

Differential with respect to β

$$\frac{\partial Z}{\partial \beta} = \sum_{i=1}^n (-E_i) e^{-\beta E_i} \cdot 1$$

$$\frac{\partial Z}{\partial \beta} = - \sum_{i=1}^n E_i e^{-\beta E_i}$$

by put the value in eq. (11)

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\bar{E} = -\frac{\partial}{\partial \beta} (\log Z)$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \cdot \frac{\partial T}{\partial T} (\log Z)$$

$$\bar{E} = -\frac{\partial T}{\partial \beta} \cdot \frac{\partial}{\partial T} (\log Z) \quad (12)$$

$$\therefore \beta = \frac{1}{KT}$$

Differential with respect to T

$$\frac{\partial \beta}{\partial T} = -\frac{1}{KT^2} \cdot 1$$

$$\frac{\partial T}{\partial \beta} = -KT^2$$

on putting value in eq. (12)

~~N.T.E.~~ $\bar{E} = KT^2 \frac{\partial}{\partial T} (\log Z) \quad (13)$

Equation (13) is called average of internal energy of system.

2: Enthalpy of system

We know that,

$$nR = nK \Rightarrow n = \text{No. of molecules}$$

K = Boltzmann Constant
R = Gas Constant

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80

from the definition of enthalpy

$$H = E + PV$$

$$\therefore E = NKT^2 \frac{\partial}{\partial T} (\log eZ)$$

(Per mole energy)

We know that

$$H = NKT^2 \frac{\partial}{\partial T} (\log eZ) + PV$$

From ideal gas equation, we have

$$PV = nRT$$

Put values

$$H = NKT^2 \frac{\partial}{\partial T} (\log eZ) + nRT$$

$$\therefore nR = NK$$

Put values,

$$H = NKT^2 \frac{\partial}{\partial T} (\log eZ) + NKT$$

Numerical :- If for the monatomic ideal gas the value of partition function is given as -

$$Z = \frac{V}{h^3} (2\pi m k T)^{3/2}$$

then calculate,

- (a) average internal energy
- (b) Enthalpy

Solution :- $Z = \frac{V}{n^3} (2\pi m k T)^{3/2}$

$$Z = \frac{V}{n^3} (2\pi m k)^{3/2} \cdot T^{3/2}$$

Let, $\frac{V}{n^3} (2\pi m k)^{3/2} = \text{constant} = \alpha$

Put values,

$$Z = \alpha T^{3/2}$$

Put value in formula of total internal energy

$$\bar{E} = k T^2 \frac{\partial}{\partial T} \log_e Z$$

$$\bar{E} = k T^2 \frac{\partial}{\partial T} \log_e (\alpha T^{3/2})$$

$$\bar{E} = k T^2 \frac{\partial}{\partial T} [\log_e \alpha + \log_e T^{3/2}]$$

$$\bar{E} = \frac{3}{2} k T^2 \cdot \frac{\partial}{\partial T} [\log_e T]$$

$$\therefore \frac{\partial \log_e \alpha}{\partial T} = 0$$

$$\bar{E} = k T^2 \cdot \frac{3}{2} \cdot \frac{1}{T} + L$$

$$\boxed{\bar{E} = \frac{3}{2} k T}$$

Per mole average internal energy

$$\boxed{\bar{E}_0 = \frac{3}{2} N k T}$$

(b) from definition of Enthalpy

$$H = \bar{E} + NKT$$

$$\bar{E}_0 = N\bar{E}$$

$$H = \bar{E}_0 + NKT$$

$$H = \frac{3}{2} NKT + NKT \quad \left(\because \bar{E}_0 = \frac{3}{2} NKT \right)$$

$$H = \frac{5}{2} NKT$$

(c) Heat Capacity

from the definition of heat capacity

$$C = \frac{\partial \bar{E}}{\partial T}$$

$$\bar{E}_0 = N\bar{E} = \frac{5}{2} NKT$$

$$C = \frac{\partial}{\partial T} \left[\frac{5}{2} NKT \right] \Rightarrow C = \frac{5}{2} NK$$

3. Heat Capacity :-

We know that from definition of heat capacity

$$C = \left(\frac{\partial \bar{E}}{\partial T} \right) \quad \textcircled{a}$$

$$C = -\frac{\partial}{\partial T} \left[\frac{\partial}{\partial \beta} (\log e_2) \right]$$

$$\left\{ \because \bar{E} = -\frac{\partial}{\partial \beta} (\log e_2) \right\}$$

$$C = -\frac{\partial}{\partial T} \cdot \frac{\partial}{\partial \beta} \cdot \frac{\partial T}{\partial T} (\log e_2)$$

$$C = -\frac{\partial T}{\partial \beta} \cdot \frac{\partial^2}{\partial T^2} (\log Z)$$

$$\because \beta = \frac{1}{kT} \Rightarrow \frac{\partial \beta}{\partial T} = \frac{-1}{kT^2}$$

Put values,

$$C = kT^2 \frac{\partial^2}{\partial T^2} (\log Z)$$

per mole heat capacity

$$C_v = NC$$

$$C_v = NkT^2 \frac{\partial^2}{\partial T^2} (\log Z)$$

A Entropy :- The physical quantity by which disorder of a system is defined is called entropy. It is denoted by S.

So, entropy of system

$$S = k \log Z(E) \quad \text{--- (1)}$$

We know that,

from the definition of partition function

$$Z = \sum_{i=1}^n e^{-\beta E_i}$$

Partition function for system - A

$$\rightarrow Z = \mathcal{N}(E) \cdot e^{-\beta E}$$

by taking log in both side

$$\log_e Z = \log [\mathcal{N}(E) \cdot e^{-\beta E}]$$

$$\log_e Z = \log \mathcal{N}(E) - \beta E$$

Multiply by k in both side

$$k \log_e Z = k \log \mathcal{N}(E) - k \beta E$$

from eq. ①

$$\therefore S = k \log \mathcal{N}(E)$$

$$\text{Then, } [S = k \log_e Z + k \beta E] \quad \text{--- (2)}$$

$$\text{Let } E = E = kT^2 \frac{\partial}{\partial T} (\log_e Z)$$

On putting value in eq. ②

$$S = k \log_e Z + k \beta \cdot kT^2 \frac{\partial}{\partial T} (\log_e Z)$$

$$S = k \log_e Z + \frac{1}{kT} k \cdot kT^2 \frac{\partial}{\partial T} (\log_e Z) \quad (\because \beta = \frac{1}{kT})$$

$$S = k \left[\log_e Z + T \frac{\partial}{\partial T} (\log_e Z) \right]$$

Per mole entropy.

$$S_0 = NS$$

$$S_0 = NK \left[\log z + T \frac{\partial}{\partial T} (\log z) \right]$$

5. Helmholtz Energy :-

We know that, from the definition of Helmholtz energy -

$$F = U - ST$$

$$\text{let } U = E$$

$$\therefore E = KT^2 \frac{\partial}{\partial T} (\log z)$$

$$\therefore S = K \left[\log z + T \frac{\partial}{\partial T} (\log z) \right]$$

on put the values,

$$F = KT^2 \frac{\partial}{\partial T} (\log z) - KT \left[\log z + T \frac{\partial}{\partial T} (\log z) \right]$$

$$F = KT^2 \frac{\partial}{\partial T} (\log z) - KT \log z - KT^2 \cdot \frac{\partial}{\partial T} (\log z)$$

$$F = -KT \log z$$

Per mole helmholtz energy

$$F_0 = NF$$

$$F_0 = -NKT \log_e Z \quad \text{--- (A)}$$

6. Gibb's Free-Enrgy :-

We know that

from the definition of Gibb's free energy

$$G = U + PV - ST \quad \text{--- (B)}$$

$$F = U - ST \quad \text{--- (C)}$$

from eqn (A) and (B)

$$q = F + PV \quad \text{--- (D)}$$

$$\therefore F_0 = -NKT \log_e Z$$

$$\therefore PV = NRT = NKT ; NR = NK$$

from eq. (C)

$$G_0 = -NKT \log_e Z + NKT$$

$$G_0 = NKT [1 - \log_e Z]$$

- Energy Distribution between Macro System

OR

Second Law of Thermodynamics

OR

Condition of Maximum Entropy

Let there are two system A and A'. Both the systems are placed in contact of heat. Due

to which exchange of heat takes place between both the system. Let energy of A and A' is E and E' respectively. Due to exchange of heat a combined system A* is formed. Let energy of combined system A* is E*.

According to energy conservation law -

$$E^* = E + E' = \text{Constant} \quad \text{--- (1)}$$

Suppose accessible state of system A is $\mathcal{N}(E)$ and accessible state of system A' and A* is $\mathcal{N}'(E')$ and $\mathcal{N}^*(E^*)$ respectively.

so, combined form of accessible state

$$\boxed{\mathcal{N}^*(E^*) = \mathcal{N}(E)\mathcal{N}'(E')} \quad \text{--- (2)}$$

We know that,

from the definition of Probability

$$P(E) \propto \mathcal{N}^*(E^*)$$

$$P(E) = C \mathcal{N}^*(E^*)$$

here, C = Proportional Constant

Put the value from eq. (2)

$$\boxed{P(E) = C \mathcal{N}(E) \mathcal{N}'(E')} \quad \text{--- (3)}$$

By taking log in both sides

$$\log P(E) = \log C + \log \mathcal{N}(E) + \log \mathcal{N}'(E')$$

Differentiate with respect to E

$$\frac{\partial}{\partial E} [\log P(E)] = \frac{\partial}{\partial E} (\log c) + \frac{\partial}{\partial E} [\log \pi(E)] + \frac{\partial}{\partial E} [\log \pi'(E')] \quad (4)$$

$\therefore c = \text{Constant}$

$$\frac{\partial}{\partial E} [\log c] = 0$$

By the Normalization condition,

$$P(E) = \text{constant} = 1(\text{max.})$$

$$\therefore \frac{\partial}{\partial E} [\log P(E)] = 0$$

by substituting value in eq. (4)

$$0 = \frac{\partial}{\partial E} [\log \pi(E)] + \frac{\partial}{\partial E} [\log \pi'(E')] \quad (5)$$

multiplying by K in both sides

$$\frac{\partial}{\partial E} [K \log \pi(E)] + \frac{\partial}{\partial E} [K \log \pi'(E')] = 0$$

$$\therefore S = K \log \pi(E) \quad \{ \text{Entropy of system-A} \}$$

$$S' = K \log \pi'(E') \quad \{ \text{Entropy of system-A'} \}$$

by substituting value

$$\frac{\partial S}{\partial E} + \frac{\partial S'}{\partial E} = 0$$

$$\frac{\partial}{\partial E} (S + S') = 0$$

$$S + S' = \text{Constant} \quad \text{--- (6)}$$

From eq. (2)

$$\Omega^*(E^*) = \Omega(E) \cdot \Omega'(E')$$

by taking log

$$\log_e \Omega^*(E^*) = \log_e \Omega(E) + \log_e \Omega'(E')$$

multiplying by K

$$K \log_e \Omega^*(E^*) = K \log_e \Omega(E) + K \log_e \Omega'(E')$$

by the definition of entropy

$$S^* = S + S' \quad \text{--- (7)}$$

from eq. (6) and (7)

$$[S^* = S + S' = \text{Constant}]$$

Again from eq. n (5)

$$\frac{\partial}{\partial E} [\log_e \Omega(E)] + \frac{\partial}{\partial E} [\log_e \Omega'(E')] = 0$$

$$\frac{\partial}{\partial E} [\log_e \Omega(E)] + \frac{\partial}{\partial E} \cdot \frac{\partial E'}{\partial E} \cdot [\log_e \Omega'(E')] = 0$$

$$\frac{\partial}{\partial E} [\log_e \Lambda(E)] + \frac{\partial E'}{\partial E} \cdot \frac{\partial}{\partial E'} [\log_e \Lambda'(E')] = 0 \quad \text{--- (8)}$$

$$\therefore \beta = \frac{\partial}{\partial E'} [\log_e \Lambda'(E')] \quad \text{--- (9)}$$

from eq. (1)

$$E^* = E + E' = \text{Constant}$$

$$E' = E^* - E$$

Differentiate with respect to E

$$\frac{\partial E'}{\partial E} = 0 - 1$$

$$\frac{\partial E'}{\partial E} = -1 \quad \text{--- (10)}$$

by substituting value in eq. (8) from eq. (9) and (10)

$$\frac{\partial}{\partial E} [\log_e \Lambda(E)] - 1 \cdot \beta = 0$$

$$\beta = \frac{\partial}{\partial E} [\log_e \Lambda(E)] \quad \text{--- (11)}$$

$$\therefore \beta = \frac{1}{K T} \quad \text{--- (12)}$$

from eq. (11) and (12)

$$\frac{1}{K T} = \frac{\partial}{\partial E} [\log_e \Lambda(E)]$$

$$\frac{1}{T} = \frac{\partial}{\partial E} [K \log_e \Lambda(E)]$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad \left\{ \because S = K \log_e \Lambda(E) \right\}$$

to write in total differential form

$$\frac{1}{T} = \frac{ds}{dE}$$

→ $ds = \frac{dE}{T}$

Above equation is second law of thermodynamics

Chapter- 4 Production of law Temperature

(I)

(a)

Joule Thomson Expansion :- In the Joule Thomson experiment, temperature of molecules of gas is done low. We know that, according to molecular physics "Intermolecular force work among the molecules. Due to this force molecules are present in bound state."

When molecules of gas are

flow in from the high pressure region to low pressure region then, molecule of gas works against the intermolecular force. Due to this work internal energy of molecule of gas becomes low. According to Boltzmann internal energy of molecule is proportional to temperature.

Tc

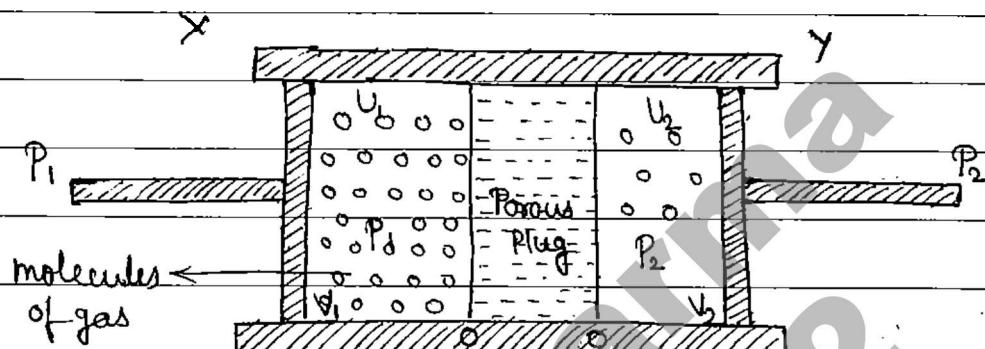
$$[E = kT]$$

That's why temperature of molecule of gas becomes low. Due to this effect cooling effect is observed.

Joule Thomson experiment is also said to be Porous-Plug experiment. Because, in the Joule Thomson experiment, flow of molecule of gas from high pressure to low pressure is takes place through the porous plug. In this experiment expansion of gas

molecule takes place, so that it is known as Joule - Thomson expansion too.

(b) Principle of Joule - Thomson Experiment :-



In the Joule - Thomson experiment, Let us consider of a device consisting piston. Suppose at the X terminal piston is P_1 and at the Y-terminal piston is P_2 . Molecules of gas are filled at the X-terminal. Now, molecules of gas are flowed from high pressure region to low pressure region by the help of porous plug. Due to which piston P_2 is moved and volume becomes V_2 to V_1 . Since the whole system is made up of thermal insulator matter, So the happening process will be adiabatic adiabatic

i.e

$$Q = \text{Constant}$$

In the differential form

$$dQ = 0 \quad \text{--- (1)}$$

(a) Work at x-terminal

By the definition of work

$$dW = PdV$$

By integrating

$$W_1 = \int_{V_1}^{V_2} P_1 dV$$

$$W_1 = -P_1 V_1 \quad \text{--- (1)}$$

(b) Work at y-terminal

$$dW = PdV$$

by integrating

$$W_2 = \int_{V_1}^{V_2} P_2 dV$$

$$W_2 = P_2 V_2 \quad \text{--- (2)}$$

$$\text{So, Total Work} = W_1 + W_2 \\ = -P_1 V_1 + P_2 V_2$$

$$dW = P_2 V_2 - P_1 V_1 \quad \text{--- (3)}$$

Suppose, internal energy of molecule of gas in initial state is U_1 and in the final state it is U_2 .

So, change in internal energy

$$dU = U_2 - U_1 \quad \text{--- (4)}$$

We know that, from the first law of thermodynamics

$$dQ = dU + dW$$

By substituting value from eq. (1), (3), (4)

(C) • Value of Joule-Thomson Coefficient :- In the Joule Thomson experiment value of enthalpy remains constant which is principle of Joule Thomson experiment. Joule Thomson coefficient is denoted by μ_H .

According to Joule-Thomson Principle

$$H = \text{Constant}$$

To write in the differential form

$$dH = 0 \quad \dots \quad (1)$$

From the definition of enthalpy

$$H = U + PV$$

Rewrite in differential form

$$dH = dU + d(PV)$$

$$dH = dU + PdV + VdP \quad \dots \quad (2)$$

From the first law of thermodynamics

$$dQ = dU + PdV \quad \dots \quad (3)$$

from the second law of thermodynamics

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

$$dQ = TdS \quad \dots \quad (4)$$

from eq. (3) and (4)

$$TdS = dU + PdV \quad \dots \quad (5)$$

by substituting value in eq. ② from eq. ⑤

$$dH = TdS + VdP$$

from eq. ①

$$0 = TdS + VdP$$

$$\boxed{ds = \frac{-Vdp}{T}} \quad \text{--- } ⑥$$

We know that entropy is function of pressure and temperature. So that value of entropy in the Joule - Thomson experiment depends upon pressure and temperature.

So, in the form of function

$$S = S(p, T)$$

To take total partial differential

$$ds = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT \quad \text{--- } ⑦$$

by put the value from eq. ⑥

$$\frac{-Vdp}{T} = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT \quad \text{--- } ⑧$$

From the fourth equation of Maxwell.

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad \text{--- } ⑨$$

by substituting value in eq. ⑧ from eq. ⑨

$$\frac{-Vdp}{T} = -\left(\frac{\partial V}{\partial T}\right)_p dp + \left(\frac{\partial S}{\partial T}\right)_p dT$$

$$-Vdp = -T \left(\frac{\partial V}{\partial T} \right)_p dp + \left(T \frac{\partial S}{\partial T} \right)_p dT$$

From the second law of thermodynamics

$$\Delta S = T \Delta S$$

then,

$$-Vdp = -T \left(\frac{\partial V}{\partial T} \right)_p dp + \left(\frac{\partial Q}{\partial T} \right)_p dT$$

$$-Vdp + T \left(\frac{\partial V}{\partial T} \right)_p dp = \left(\frac{\partial Q}{\partial T} \right)_p dT$$

$$\left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp = \left(\frac{\partial Q}{\partial T} \right)_p dT \quad \text{--- (10)}$$

from the definition of heat capacity

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p \quad (\text{Heat capacity at con. pressure})$$

Put the value in eq. (10)

$$\left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp = C_p dT$$

M.T.R

$$M.T.R = \left(\frac{dT}{dP} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] \quad \text{--- (11)}$$

Equation (11) is known as Joule-Thomson equation

Case-I :- Joule-Thomson Coefficient for ideal gas -

We know that, from ideal gas equation -

$$PV = RT \quad \text{--- (2)}$$

Differential with respect to T , $P = \text{Constant}$

$$P \left(\frac{\partial V}{\partial T} \right)_P = R \cdot 1$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} \quad \text{--- (3)}$$

from eq. (1),

$$PV = RT$$

$$\frac{V}{T} = \frac{R}{P} \quad \text{--- (4)}$$

from eq. (3) and (4)

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{V}{T} \quad \text{--- (5)}$$

Again we know that

from Joule-Thomson coefficient

$$M_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad \text{--- (6)}$$

on putting value from eq. (5)

$$M_H = \frac{1}{C_p} \left[T \cdot \frac{V}{T} - V \right]$$

$$M_H = 0 \quad \text{--- (7)}$$

Hence, it is clear from eq (6) that value of Joule-Thomson coefficient is zero for the ideal gas.

Therefore, Joule-Thomson experiment does not observe for ideal gas.

Case-II Joule-Thomson Coefficient for Real Gas -

We know that, Equation for real gas from Vanderwaal equation

$$\left(p + \frac{a}{V^2}\right)(V-b) = RT \quad \text{(B)}$$

Where, a = Pressure constant
 b = Volume constant

$$p + \frac{a}{V^2} = \frac{RT}{(V-b)}$$

Diffr. with respect to T , $p = \text{constant}$

$$0 + a\left(-\frac{2}{V^3}\right)\left(\frac{\partial V}{\partial T}\right)_p = R \cdot \left[1 - \frac{1}{(V-b)} - T \frac{1}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_p\right]$$

$$\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{(V-b)}$$

$$\frac{RT}{(V-b)^2} \left[1 - \frac{2(V-b)^2 a}{RT V^3}\right] \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{(V-b)}$$

$$\frac{T\left(\frac{\partial V}{\partial T}\right)_p}{V-b} = \frac{1 - 2a(V-b)^2}{RT V^3}$$

Since, $V \gg b$ { by neglecting high power of b with respect to V }

then,

$$\frac{T\left(\frac{\partial V}{\partial T}\right)_p}{V-b} = \left[1 - \frac{2a(V-b)^2}{RT V^3}\right]$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = \frac{V-b}{[1 - \frac{\alpha a}{RTV}]} \quad (1)$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = (V-b) \left[1 - \frac{\alpha a}{RTV} \right]^{-1}$$

From the Binomial theorem

$$(1+nx)^{-n} = 1-nx$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = (V-b) \left[1 + \frac{\alpha a}{RTV} \right]$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = V-b + \frac{\alpha a V}{RTV} = \frac{\alpha a b}{RTV}$$

$$T \left(\frac{\partial V}{\partial T} \right)_P = V-b + \frac{\alpha a}{RT} - \frac{\alpha a b}{RTV}$$

by neglecting the term $\frac{\alpha a b}{RTV}$

$$T \left(\frac{\partial V}{\partial T} \right)_P = V-b + \frac{\alpha a}{RT} \quad (19)$$

Again we know that,

from the Joule-Thomson coefficient

$$\mu_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad (20)$$

by substituting value in eq. (20) from eq. (19)

$$\mu_H = \frac{1}{C_P} \left[V-b + \frac{\alpha a}{RT} - V \right]$$

$$\boxed{\mu_H = \frac{1}{C_P} \left[\frac{\alpha a}{RT} - b \right]} \quad (21)$$

It is clear from eq. (2) that Joule-Thomson coefficient is find for real gas. So, Joule-Thomson experiment observed for real gas.

(d) Result of Joule-Thomson Experiment

We know that, Joule Thomson coefficient for real gas -

$$\mu_h = \frac{1}{R} \left[\frac{2a}{RT} - b \right] \quad \text{--- (1)}$$

Case-i If $\frac{2a}{RT} - b = 0$

$$\frac{2a}{RT} = b$$

HFR

$$T_i^{\circ} = \frac{2a}{Rb}$$

②

Equation ② denotes Inverse Temperature.

At the inversion temperature, Joule-Thomson experiment does not work because, value of Joule-Thomson coefficient find be zero. Which is find for ideal gases.

Case-ii If $\frac{2a}{RT} > b$

$$\frac{2a}{Rb} > T$$

$$T_i^{\circ} > T$$

{from eq. ②}

③

from eq. ①

$$u_H = +ve \quad \text{--- } ④$$

it is clear from eq. ③ and ④ that when temperature of molecule of gas (T) is less than inversion temperature (T_0) then, value of u_H is obtains positive. Which defines cooling effect which is property of Joule-Thomson experiment.

Case-iii

$$\text{If } \frac{\partial a}{RT} < b$$

$$\frac{\partial a}{Rb} \leftarrow T$$

from eq. ②

$$T_0 < T \quad \text{--- } ⑤$$

from eq. ①,

$$u_H = -ve \quad \text{--- } ⑥$$

It is clear from eq. ⑤ and ⑥, When temperature of gas molecule (T) is greater than inversion temperature (T_0) then, value of u_H will be negative. Due to which heating effect occurs. Which is inversion of Joule-Thomson experiment.

(e) Important Numericals of Joule-Thomson Experiment

Q.1

$$R = 8.31 \text{ J/Kmol} ; \alpha = 1.32 \text{ Nm}^4/\text{mol}^2$$

$$b = 3.12 \times 10^{-5} ; T_i = ?$$

Solution We know that, Temperature of inversion

$$T_i = \frac{2a}{2b}$$

$$T_i = \frac{2 \times 1.32}{8.4 \times 3.12 \times 10^{-5}}$$

$$T_i = 1007 \text{ K}$$

Q.2

Given : $T = 400 \text{ K}$, $C_p = 29.25 \text{ J/mol}$
 $\alpha = 0.132 \text{ Nm}^4/\text{mol}^2$, $R = 8.4 \text{ J/(K-mol)}$, $\mu_H = ?$

Solution :- Joule Thomson coefficient -

$$\mu_H = \frac{1}{C_p} \left(\frac{\partial q}{\partial P} - b \right)$$

$$\mu_H = \frac{1}{29.25} \left(\frac{2 \times 0.132}{8.4 \times 400} - 3.12 \times 10^{-5} \right)$$

$$\mu_H = \frac{1}{29.25} \left(7.35 \times 10^{-5} - 3.12 \times 10^{-5} \right)$$

$$\mu_H = \frac{4.83 \times 10^{-5}}{29.25}$$

$$\Rightarrow \mu_H = 1.65 \times 10^{-6} \text{ km}^2/\text{N}$$

Q.3

$$T = 300 \text{ K}, C_p = 36.69 \text{ J/mol-K}$$

$$\alpha = 1.36 \text{ Nm}^4/\text{mol}^2$$

$$b = 4.267 \times 10^{-5} \text{ m}^3/\text{mol}$$

$$\mu = ? \quad T_i = ?$$

Solution :- Joule-Thomson coefficient

$$\mu_H = \frac{1}{C_p} \left(\frac{\partial q}{RT} - b \right)$$

$$\mu_H = \frac{1}{36.69} \left(\frac{29 \times 0.36}{8.4 \times 300} - 4.267 \times 10^{-5} \right)$$

$$= \frac{1}{36.69} \left(28.57 - 4.267 \times 10^{-5} \right) \times 10^{-5}$$

$$= \frac{24.23 \times 10^{-5}}{86.39}$$

$$[\mu_H = 6.6 \times 10^{-6} \text{ km}^2/\text{N}]$$

Temperature of Inversion

$$T_i = \frac{2a}{Rb}$$

$$T_i = \frac{2 \times 3.6}{8.4 \times 4.267 \times 10^{-5}}$$

$$[T_i = 2008.9 \text{ K}]$$

Q. 4

$$T = 300 \text{ K} ; C_p = 29.4 \text{ J/mol}$$

$$R = 8.4 \text{ J/Kmol}, a = 0.132 \frac{\text{Nm}^2}{\text{mol}^2}$$

$$b = 3.12 \times 10^{-5} \text{ m}^3/\text{mol}, \mu_H = ?$$

Solution Joule Thomson Coefficient

$$\mu_H = \frac{1}{C_p} \left(\frac{\partial q}{RT} - b \right)$$

$$\begin{aligned}
 M_H &= \frac{1}{29.4} \left(\frac{\alpha \times 0.132}{8.4 \times 300} - 3.12 \times 10^{-5} \right) \\
 &= \frac{1}{29.4} (10.47 \times 10^{-5} - 3.12 \times 10^{-5}) \\
 &= \frac{7.35 \times 10^{-5}}{29.4} \\
 \boxed{M_H = 0.25 \times 10^{-5}}
 \end{aligned}$$

Q.5

$$a = 0.0247 \text{ Nm}^4/\text{mol}^2 ; b = 2.56 \times 10^{-5}$$

$$R = 8.4 \text{ J/Kmol} ; (p = 20.5 \text{ J/mol})$$

$$T = 100\text{K} ; M_H = ? , T_i = ?$$

Solution :- Temperature of Inversion

$$T_i^\circ = \frac{2a}{Rb}$$

$$= \frac{2 \times 0.0247}{8.4 \times 2.56 \times 10^{-5}} = \frac{0.0494}{8.4 \times 2.56 \times 10^{-5}}$$

$$\boxed{T_i^\circ = 232.5 \text{ K}}$$

Joule - Thomson coefficient

$$M_H = \frac{1}{C_p} \left(\frac{\partial a}{R_T} - b \right)$$

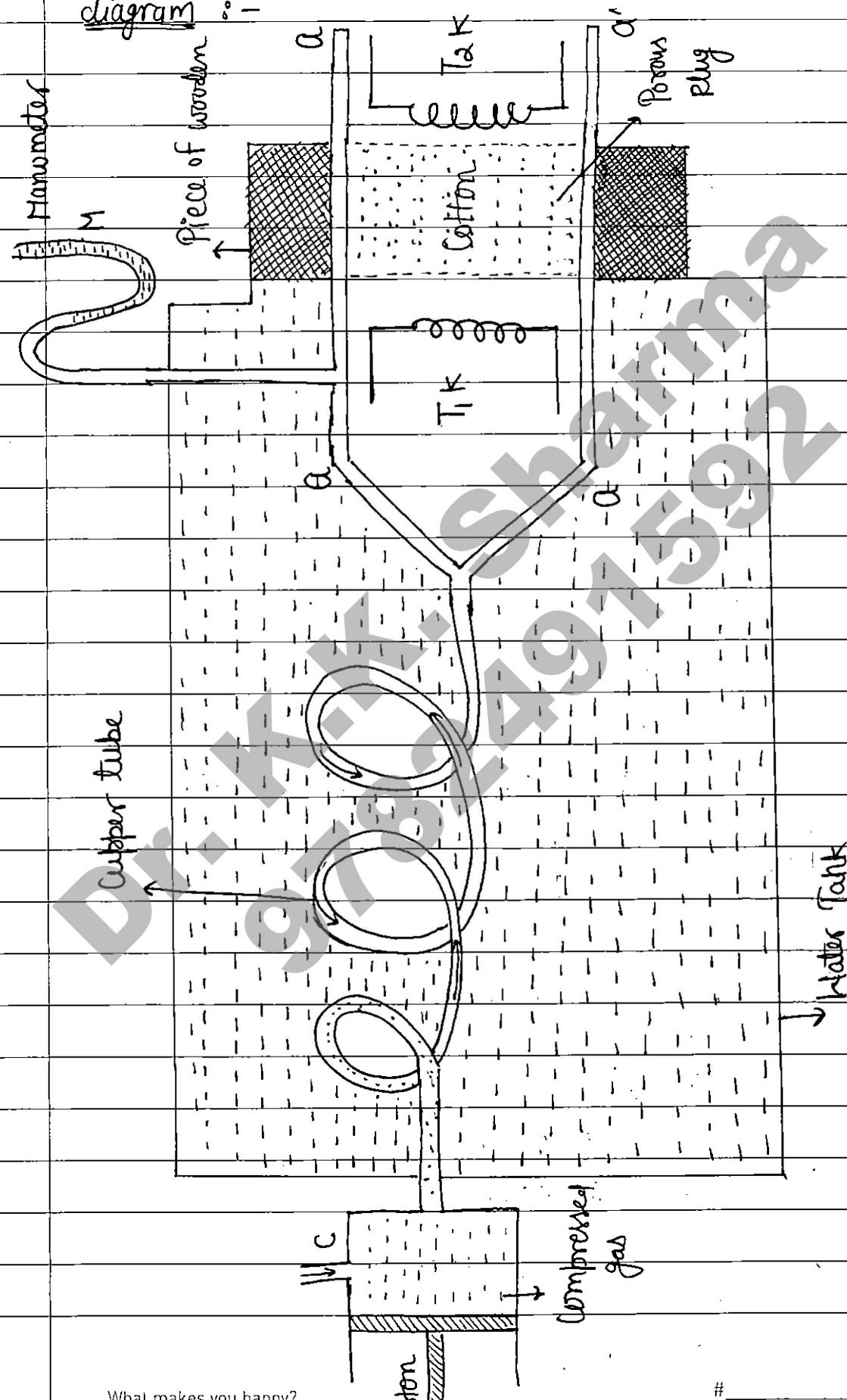
$$M_H = \frac{1}{20.5} \left(\frac{2 \times 0.0247}{8.4 \times 100} - 2.56 \times 10^{-5} \right)$$

$$M_H = \frac{1}{20.5} (5.88 - 2.56) \times 10^{-5}$$

$$\boxed{M_H = 0.16 \times 10^{-5}}$$

(F)

Explanation of Joule-Thomson experiment with diagram :-



Toule-Thomson experiment only works for real gases.
It do not observed for ideal gases.

In the Joule Thomson experiment a device consisting a piston is used. Gas is compressed by this piston. A copper tube is connected by this piston. After compressing by piston gas passes through this tube. This tube is connected to a other tube air. In the other tube such type of arrangement so that it can measure pressure and temperature. To measure the temperature of molecule of gas two thermometers T_1 & T_2 are also connected. To measure the pressure a manometer is connected to same tube. A porous plug is connected to this tube. This porous plug is kept between two pieces of wood so that this can be present in rest state. Gas molecules flows from high pressure region to low pressure region through this porous plug. Due to which expansion of gas molecules takes place. And due to this expansion cooling effect observed. Whole arrangement kept in a water tank so that it cannot be influence by environment. It is called arrangement of Joule-Thomson experiment.

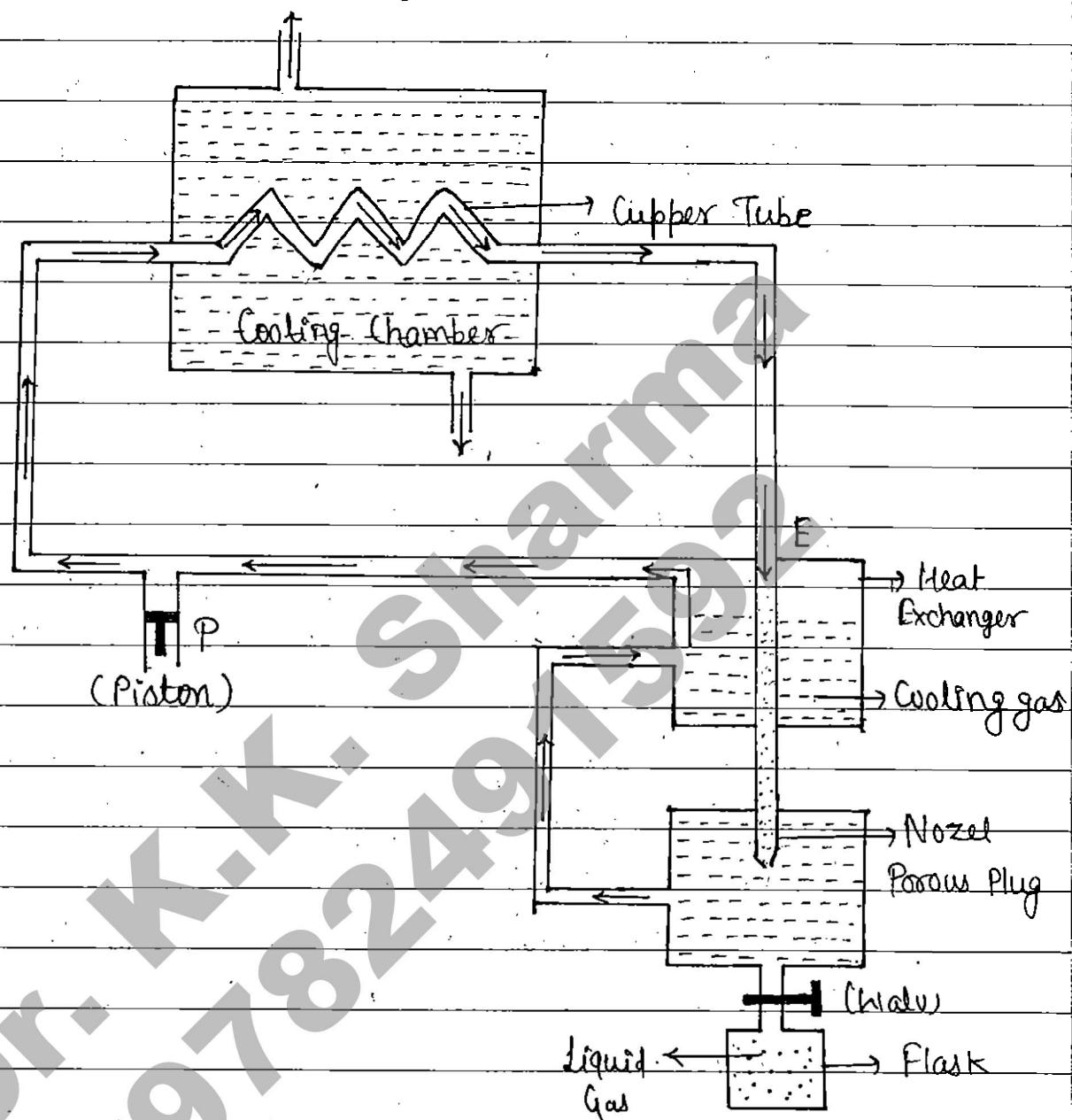
II Regenerating Cooling Method

OR

Feedback Cooling Method

By the Regenerating cooling method, cooling effect is divert in the gas molecule. This method works on the principle of Joule-Thomson experiment. We know that, in the Joule-Thomson experiment, gas molecule is flowed from high pressure region to low pressure region through the free porous plug. Similarly, in regenerating cooling method gas molecule flow from high pressure region to low pressure region. But in the Joule-Thomson experiment gas molecule can't be changed in liquid state. In the regenerating cooling method gas molecule is again and again.

Explanation with Diagram :-



In the regenerating cooling method, a device fitted with a piston is used. Gas molecules are compressed by this piston and after compressing these molecules of gas reach to the cooling chamber through the tube. Temperature of molecule of gas present in cooling chamber is lower than the

temperature of gas molecule present in tube. Therefore, in the cooling chamber exchange of heat takes place among the gas molecules. Due to which temperature of gas molecule present in the tube decreases.

Now, these molecules of gas reach to the nozzle-porous plug from the cooling chamber. Molecules of gas are allowed to expand from high pressure region to low pressure region through the porous plug. Therefore, expansion of gas molecule takes place. And we know that when expansion of gas molecule takes place then internal energy of molecule decreases. Due to which temperature of gas molecule also decreases. But it is not so much low that it can be converted into liquid. That's why gas molecule reach to the heat exchanger E by the feedback technique.

Now, this process has repeated again and again until the gas molecule converted into liquid. When molecules of gas are converted into liquid they are collected into a flask through the valve. This method by which temperature of gas molecule is decreased, is called regenerative cooling method.

• Efficiency of Regenerating Cooling method

We know that, regenerating cooling method, works on the principle of Joule-Thomson experiment. In Joule-Thomson experiment value of enthalpy remains constant therefore value of enthalpy also will be constant in the regenerating cooling method.

According to energy conservation law, before reaction and after reaction total energy remains constant.

Suppose enthalpy of the molecule of gas in the initial condition is h_i . Let x part of the molecule of gas is converted into liquid, and enthalpy of this part is h_e . and in the final position (remaining-part) enthalpy is h_f .

Now according to enthalpy conversation law -

$$h_i = x h_e + (1-x) h_f$$

$$h_i = x h_e + h_f - x h_f$$

$$h_i - h_f = x(h_e - h_f)$$

$$x = \frac{h_f - h_i}{h_e - h_f}$$

①

Equation ① denotes the efficiency of regenerating cooling method. It is also termed as performance coefficient.

1. Given :- $h_i = 90 \text{ cal.}$; $h_f = 120 \text{ cal.}$
 $h_e = 50 \text{ cal.}$; $x = ?$

Solution: We know that

$$x = \frac{h_f - h_i}{h_f - h_e}$$

on putting value

$$x = \frac{120 - 90}{120 - 50} = \frac{30}{70}$$

$$\boxed{x = 0.42}$$

2. Given :- $h_i = 80 \text{ cal.}$ $h_f = 120 \text{ cal.}$
 $h_e = 60 \text{ cal.}$ $x = ?$

Solution We know that,

$$x = \frac{h_f - h_i}{h_f - h_e} \times 100\%$$

$$x = \frac{120 - 80}{120 - 60} \times 100\%$$

$$x = \frac{40}{60} \times 100\%$$

$$\boxed{x = 66.67\%}$$

- III • Cooling by Adiabatic Expansion :- By the adiabatic expansion cooling method temperature of molecule

of gas has decreased. In the adiabatic expansion cooling method thermal insulator matter is used. In this method, a porous plug is connected because this method also works on Joule-Thomson experiment. Therefore, molecule of gas is flowed from high pressure region to low pressure region through the porous-plug. Due to this effect expansion of gas-molecule takes place. When expansion of gas molecule takes place then it have to do work against the inter-molecular force. And due to this work internal energy of molecule of gas decreases. According to the Boltzmann, internal energy of molecule of gas is proportional to temperature ($E = kT$). That's why temperature of gas molecule is decreases. Due to use of thermal insulator matter in this method the happening process is adiabatic. The method by which temperature of gas molecule is decrease is called Adiabatic expansion cooling method.

Let the pressure on the molecule of gas is P_i in the initial condition and temperature is T_i and in the final position pressure and temp. are P_f and T_f respectively.

From the adiabatic state equation

$$T^{\gamma} = \text{Const.} \quad (\text{between pressure \& Temp.})$$

for initial condition

$$T_i \cdot P_i^{\frac{1-y}{y}} = \text{const.} \quad \textcircled{1}$$

for final condition

$$T_f \cdot P_f^{\frac{1-y}{y}} = \text{const.} \quad \textcircled{2}$$

from eq. ① and ②

$$T_i \cdot P_i^{\frac{1-y}{y}} = T_f \cdot P_f^{\frac{1-y}{y}}$$

$$T_f = T_i \left(\frac{P_i}{P_f} \right)^{\frac{1-y}{y}} \quad \textcircled{3}$$

By the help of eqn ③ final temperature of gas molecule can be calculated.

For example

For gas molecule of CO_2

$$T_i = 300\text{K} \quad P_i = 150 \text{ atm}$$

$$P_f = 1 \text{ atm} \quad T_f = ? \quad f = 1.3$$

We know that, $T_f = T_i \left(\frac{P_i}{P_f} \right)^{\frac{1-y}{y}}$

$$T_f = 300 \left(\frac{150 \text{ atm}}{1 \text{ atm}} \right)^{\frac{1-1.3}{1.3}}$$

$$T_f = 300 \left(\frac{150}{1} \right)^{-\frac{0.3}{1.3}}$$

$$T_f = \frac{300}{(150)^{3/13}}$$

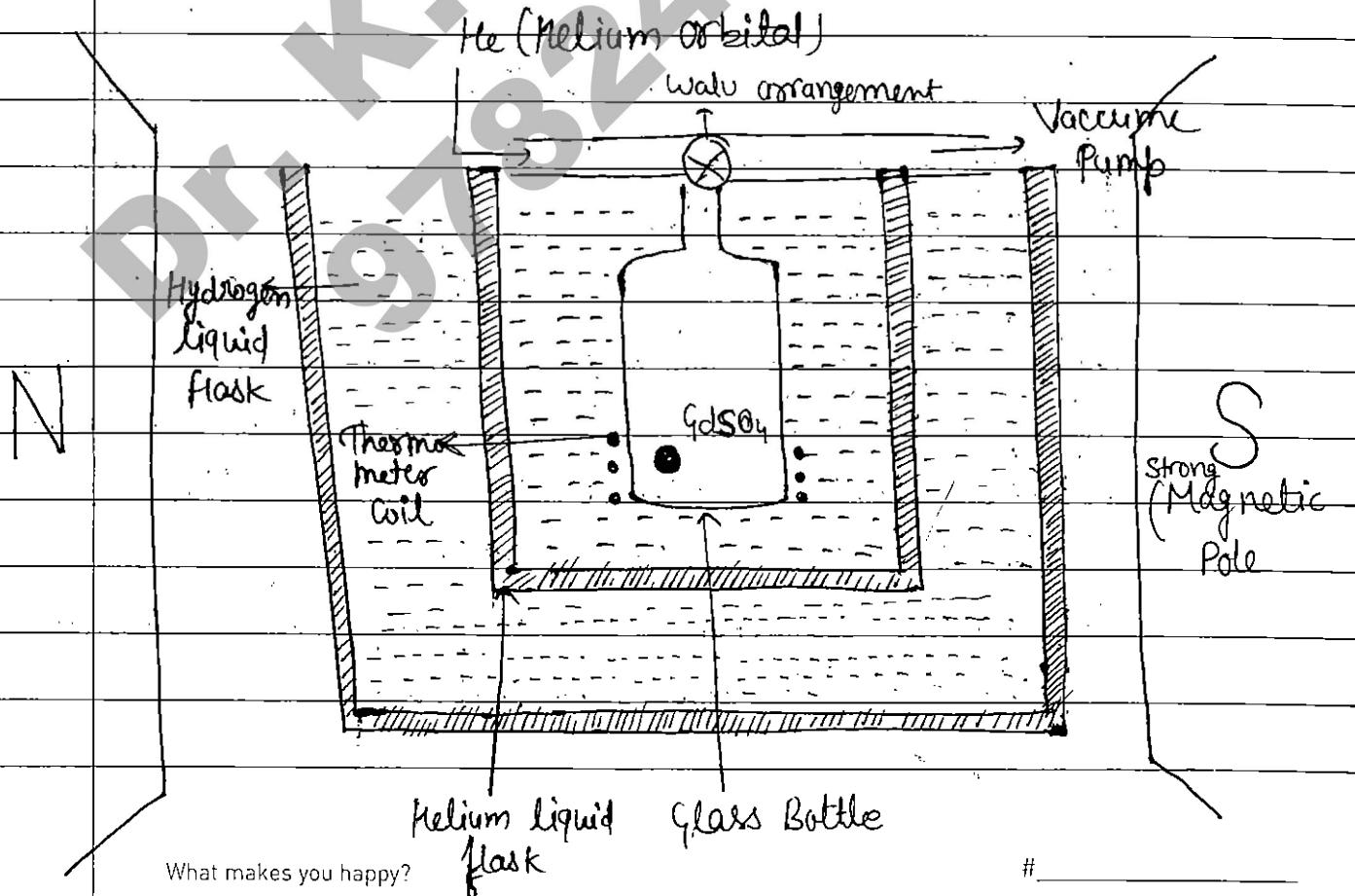
$$T_f = 96\text{ K}$$

That's why CO_2 gas is called dry ice.

N Cooling by Adiabatic demagnatization

With the Joule-Thomson experiment the temperature of gas molecule can be decreased till 0.82 K . While by adiabatic demagnatization the temperature of gas molecule can be obtained till 10^{-3} K . In the adiabatic demagnatization method paramagnetic salt is used. GdSO_4 (gadolinium sulphate) is used in the form of paramagnetic salt.

Explanation with Diagram :-



(Coaxial solenoid coil)

In the adiabatic demagnetization cooling method, we take a glass bottle which is connected by a helium orbital and this bottle is connected to a vacuum pump through a valve.

Now, we fill paramagnetic salt in the glass bottle. Gd₂SO₄ is used as paramagnetic salt. To measure the temperature of this paramagnetic salt thermometer coil is connected. This glass bottle is placed in a flask filled with helium liquid. To make adiabatic process it is again placed in a other flask filled with hydrogen liquid so that Gd₂SO₄ can not come to the contact with environment. This whole arrangement is kept between strong magnetic pole.

In the glass bottle He-liquid is allow to flow from helium-orbital so that paramagnetic salt Gd₂SO₄ come to the equilibrium condition. Now, we apply strong magnetic field. According to Curie's law ($\chi = C/T$) after applying strong magnetic field temp. of paramagnetic salt increases. Due to which helium liquid converts into ^{gas} liquid. Now we take out of He-liquid and He-gas form the bottle by the vacuum pump and vacuum is diverted in the glass bottle.

Now, strong magnetic field is removed suddenly ($B=0$) due to which demagnetization of paramagnetic salt $\text{Gd}_{0.9}\text{S}_{0.1}$ takes place and due to this demagnetization temperature of paramagnetic salt $\text{Gd}_{0.9}\text{S}_{0.1}$ decreases [because, due to demagnetization expansion takes place among the molecules of $\text{Gd}_{0.9}\text{S}_{0.1}$] This temperature is obtained 10^{-3} K . Which is measured by the thermometer coil.

- Mathematical Analysis - We know that in the thermodynamic physics there are four thermodynamic coordinates (P, V, T, S) In adiabatic demagnetization (thermodynamics magnetic physics) the coordinates are (B, I, T, S).

Work done by paramagnetic salt

$$dW = PdV$$

In demagnetization physics

$$P \rightarrow -B, \quad V \rightarrow I$$

on putting value

$$[dW = -BdI] \quad \text{--- (1)}$$

We know that,

From the first law of thermodynamics

$$dQ = dU + dW$$

from eq (1),

$$dQ = dU - BdI \quad \text{--- (2)}$$

From the third equation of Maxwell

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

$$P \rightarrow -B, V \rightarrow I$$

On Putting value

$$+\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_B \quad \text{--- (3)}$$

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(T \cdot \frac{\partial I}{\partial S}\right)_B \quad \text{--- (4)}$$

From second law of thermodynamics

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

In partial differentiation form

$$T dS = dQ$$

on putting value in eq. (4)

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(T \cdot \frac{\partial I}{\partial Q}\right)_B$$

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(T \cdot \frac{\partial I}{\partial Q} \cdot \frac{\partial Q}{\partial T}\right)_B$$

$$\left(\frac{\partial T}{\partial B}\right)_S = -T \cdot \left(\frac{\partial I}{\partial T}\right)_B \left(\frac{\partial Q}{\partial T}\right)_B \quad \text{--- (5)}$$

We know that from the definition of heat capacity

$$C_B = \left(\frac{\partial Q}{\partial T}\right)_B \quad [\text{At Constant magnetic field}]$$

on putting value in eq. ⑤

$$\left(\frac{\partial T}{\partial B}\right)_S = -T \frac{C}{C_B} \left(\frac{\partial I}{\partial T}\right)_B \quad \text{--- } ⑥$$

Again, we know that from the Ohm's law

$$I = \frac{C}{T} \quad \text{--- } ⑦$$

$$I = \frac{T}{H} \quad \text{--- } ⑧$$

$$B = \mu_0 H \quad \text{--- } ⑨$$

from eq. n ⑦ and ⑧

$$\frac{I}{H} = \frac{C}{T}$$

$$I = \frac{CH}{T}$$

on substituting value from ⑨

$$I = \frac{C_B}{\mu_0 T}$$

Dif. with respect to T, B = Constant

$$\left(\frac{\partial I}{\partial T}\right)_B = -\frac{C_B}{\mu_0 T^2}$$

on putting value in eq. ⑥

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{T C_B}{C_B \mu_0 T^2} \quad \text{--- } ⑩$$

Let $\frac{C}{M_0} = A = \text{Constant}$

on putting value in eq. ⑩

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{AB}{C_B T} \quad \text{--- (11)}$$

Equation ⑪ is a single order differential equation so, its solution will by ~~sep~~ variable separation method,

so, by variable separation method

$$T dT = \frac{A}{C_B} B dB$$

on integrating

$$\int_{T_1}^{T_2} T dT = \frac{A}{C_B} \int_B^0 B dB$$

$$\int_{2T_1}^{T_2} \frac{T^2}{2} dT = \frac{A}{C_B} \int_B^0 \frac{B^2}{2} dB$$

$$T_2^2 - T_1^2 = \frac{A}{C_B} (-B^2)$$

$$T_2^2 - T_1^2 = \frac{AB^2}{C_B}$$

$$T_2 = T_1 \left[1 - \frac{AB^2}{C_B T_1^2} \right]^{1/2} \quad \text{--- (12)}$$

By the help of eq. (12) temperature in adiabatic demagnetization method.

Numericals

Q.1

Given: $T_1 = 3\text{K}$; $B = 1\text{T}$

$$A = 600 \frac{\text{J}\cdot\text{K}}{\text{kg}\cdot\text{T}^2}$$

$$C_B = 420 \text{ J/Kg}\cdot\text{K}$$

$$T_2 = ?$$

Solution :- We know that, from adiabatic demagnetization method

$$T_2 = T_1 \left[1 - \frac{AB^2}{C_B T_1^2} \right]^{1/2}$$

on putting value,

$$T_2 = 3 \left[1 - \frac{600 \times (1)^2}{420 \times (3)^2} \right]^{1/2}$$

$$T_2 = 3 \left[1 - \frac{60}{42 \times 9} \right]^{1/2}$$

$$T_2 = 3 \left[1 - \frac{60}{378} \right]^{1/2}$$

$$T_2 = 3 \left[\frac{318}{378} \right]^{1/2}$$

$$T_2 = 3(0.8412)^{1/2}$$

$$T_2 = 3 \times 0.917$$

$T_2 = 2.75\text{K}$

Q.2

$$\text{Given:- } T_1 = 2\text{K} \quad A = 42 \frac{\text{J}}{\text{kg}\cdot\text{K}}$$

$$T_2 = 1\text{K}$$

$$B = ? \quad C_B = 420 \frac{\text{J}}{\text{kg}\cdot\text{K}}$$

Solution:- We know that,
from adiabatic demagnetization

$$T_2 = T_1 \left[1 - \frac{AB^2}{C_B T_1^2} \right]^{1/2}$$

On putting values

$$1 = 2 \left[1 - \frac{42B^2}{420(2)^2} \right]^{1/2}$$

by doing square both side.

$$1 = 4 \left[1 - \frac{B^2}{40} \right]$$

$$10 = 40 - B^2$$

$$B^2 = 30$$

$$B = \sqrt{30} \Rightarrow B = 5.47 \text{ T}$$

Distribution law of molecular velocity

- Maxwell's Distribution law of molecular velocity :-

According to Maxwell's distribution law of molecular velocity. At the constant temperature root mean square velocity of gas molecule is equal to those number of molecule which lies in constant range of velocity.

- Hypothesis of Maxwell

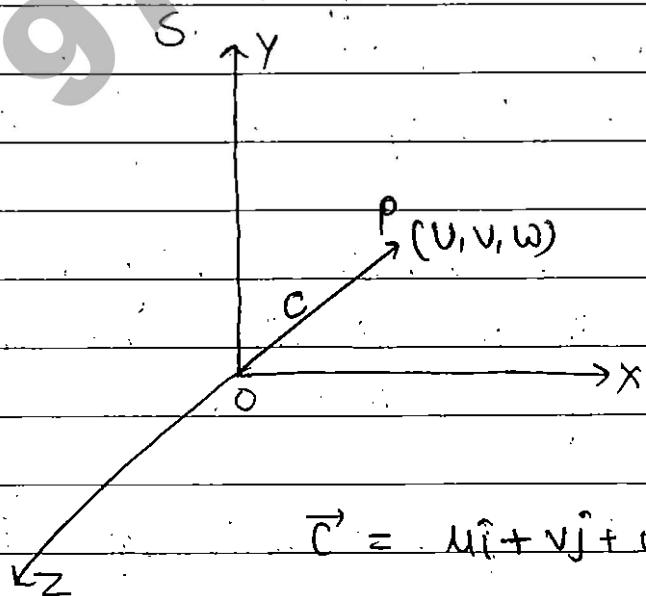
1. According to Maxwell elastic collision takes place among the gas molecules.
2. After collision, molecules of gas do.
3. Molecules of gas applies force on each other only in the state of collision i.e. force do not works on gas molecule except state of collision.
4. According to maxwell velocity of molecules of gas is possible in all direction. and every velocity is possible of gas-molecules.
5. Distribution of molecules is equal in a gas. According

to Maxwell for the same gas (like helium) size of molecule and mass of molecule are find be equal.

f. This size of molecules of gas is negligible in comparison to distance between the molecules of gas.

g. No. of molecules is find be in majority in the finite value of volume.

- Mathematical Analysis - Let velocity of gas molecule in x-direction is u and probability function of velocity is $f(u)$ in x-dirn. and in the y-direction velocity and probability function are v and $f(v)$ respectively and velocity in z-direction is w so, the probability function in z-direction is $f(w)$.
Let the magnitude of velocity is c .



$$c^2 = u^2 + v^2 + w^2 \quad \text{--- (1)}$$

Let the change in magnitude of velocity is c to $c+dc$
then change in velocity in x -direction is u to $u+du$
and change in velocity in y -direction and z -
direction is v to $v+dv$ and w to $w+dw$ respectively.

Probability of molecule in u and $u+du$ velocity
range = $f(u) du$

Probability of molecule in v and $v+dv$ velocity
range = $f(v) dv$

Probability of molecule in w and $w+dw$ velocity
range = $f(w) dw$

According to principle of probability, combined
probability will be

$$P(u, v, w) = f(u) f(v) f(w) du dv dw \quad \text{--- (2)}$$

Let no. of molecule present in per unit volume is n .

so, no. of molecule present in c and $c+dc$
velocity range = Probability $\times n$

$$dn = n \times P(u, v, w)$$

put the value from eq. (2), we have

$$dn = n f(u) f(v) f(w) du dv dw \quad \text{--- (3)}$$

According to Maxwell, density of the gas molecule

Can be calculated by the velocity indicator diagram. Now moving particles are dotted in the graph (on the basis of velocity). This graph is known as 'velocity indicator graph' of Maxwell.

so velocity density

$$\rho = \frac{dn}{dV dV d\omega}$$

substituting value from eq. ③

$$\rho = \frac{n f(v) f(v) f(\omega)}{dV dV d\omega}$$

$$\boxed{\rho = n f(v) f(v) f(\omega)} \quad \text{--- (4)}$$

Now, velocity density (ρ) and resultant velocity of c is consider to be constant in definite velocity range and it can be solve by Langrang's Method.

from eq. ①

$$c^2 = v^2 + v^2 + \omega^2$$

to write in differential form

$$0 = 2vdv + 2vdv + 2\omega d\omega$$

$$0 = 2(vdv + vdv + \omega d\omega)$$

since $v \neq 0$

$$\boxed{vdv + vdv + \omega d\omega = 0} \quad \text{--- (5)}$$

from eq. (4), $\rho = n f(v) f(v) f(\omega)$

by differentiation

$$0 = d[nf(v) f(u) f(w)]$$

$$0 = \cancel{d}[f(v) f(u) f(w)]$$

$\Rightarrow n \neq 0$ {no. of molecules in per unit volume}

$$0 = f(v)f(w) df(u) + f(u)f(w) df(v) + f(u)f(v) df(w)$$

To write in partial differentiation form,

$$0 = f(v)f(w) \frac{\partial f(u)}{\partial u} du + f(u)f(w) \frac{\partial f(v)}{\partial v} dv + f(u)f(v) \frac{\partial f(w)}{\partial w} dw$$

divide by $f(v)f(u)f(w)$

$$0 = \frac{f(v)f(w)}{f(u)f(v)f(w)} \frac{\partial f(u)}{\partial u} + \frac{f(u)f(w)}{f(v)f(v)f(w)} \frac{\partial f(v)}{\partial v} + \frac{f(u)f(v)}{f(u)f(v)f(w)} \frac{\partial f(w)}{\partial w}$$

$$\boxed{0 = \frac{1}{f(u)} \frac{\partial f(u)}{\partial u} + \frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + \frac{1}{f(w)} \frac{\partial f(w)}{\partial w}} \quad \textcircled{5}$$

Eq'n (5) and (6) are not general differentiation equation
therefore, these differential equation can be solved
by Langrange's method.

\Rightarrow Langrange's Method :- In this method a constant is used. Let this constant is β . then multiplying by

β in eq. ⑤

$$\beta [vdv + vdv + wdw] = 0 \quad \text{--- } ⑦$$

by adding eq. ⑥ and ⑦

$$\Rightarrow 0 = \left[\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} dv + \frac{1}{f(v)} \frac{\partial f(v)}{\partial v} dv + \frac{1}{f(w)} \frac{\partial f(w)}{\partial w} dw \right] +$$

$$\beta [vdv + vdv + wdw]$$

$$\Rightarrow 0 = \left(\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + \beta v \right) dv + \left(\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + \beta v \right) dv +$$

$$\left(\frac{1}{f(w)} \frac{\partial f(w)}{\partial w} + \beta w \right) dw$$

$$\Rightarrow \left(\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + \beta v \right) dv + \left(\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + \beta v \right) dv + \left(\frac{1}{f(w)} \frac{\partial f(w)}{\partial w} + \beta w \right) dw$$

$$= 0 \cdot dv + 0 \cdot dv + 0 \cdot dw$$

by the comparison of the coefficient of dv, dv, dw

Now $\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + \beta v = 0$

by the variable separation method

$$\int \frac{\partial f(v)}{f(v)} = - \int \beta v dv$$

$$\log_e f(v) = -\frac{\beta v^2}{2} + \log_e a \quad \left\{ \begin{array}{l} \log_e a = \text{Integration} \\ \text{Constant} \end{array} \right.$$

$$\log_e \left(\frac{f(v)}{a} \right) = -\frac{\beta v^2}{2}$$

by taking antilog

$$\frac{f(u)}{a} = e^{-\frac{\beta u^2}{2}}$$

$$\boxed{f(u) = a e^{-\frac{\beta u^2}{2}}} \quad \text{--- (8)}$$

similarly, $f(v) = a e^{-\frac{\beta v^2}{2}}$ } --- (9)

$$f(w) = a e^{-\frac{\beta w^2}{2}}$$

on substituting value in eq. (9) from eq. (8) and (9)

$$P = n a^3 e^{-\frac{\beta u^2}{2}} e^{-\frac{\beta v^2}{2}} e^{-\frac{\beta w^2}{2}}$$

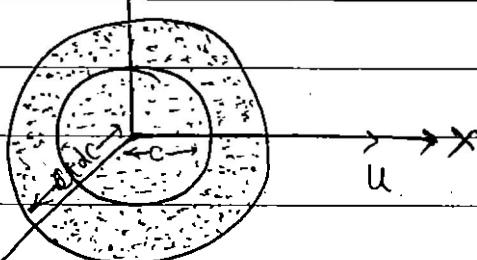
$$P = n a^3 e^{-\frac{\beta}{2}(u^2 + v^2 + w^2)}$$

$$P = n a^3 e^{-\frac{\beta C^2}{2}} \quad \{ \text{By eq. (1)} \}$$

Let $\frac{\beta}{2} = b =$ (another constant)

$$\boxed{P = n a^3 e^{-b C^2}} \quad \text{--- (10)}$$

a and b in eq. (10) are constant.



so, small volume

$$V = \frac{4}{3} \pi C^3$$

diff. with respect to c

$$\frac{dV}{dc} = \frac{4}{3}\pi 3c^2 \cdot 1$$

$$dV = 4\pi c^2 dc \quad \text{--- (11)}$$

so, no. of molecules present in small volume

$$dn_c = pdV$$

by eq. (10) and (11)

$$dn_c = 4\pi c^2 n a^3 e^{-bc^2} dc \quad \text{--- (12)}$$

Eq. (12) is called Maxwell's distribution law of molecular velocity.

Value of Constants

(1) Value of constant 'a'

Let the no. of molecules present in per unit volume is n

so, total no. of molecule

$$\rightarrow n = \int_0^\infty dn_c$$

from eq. (12)

$$n = \int_0^\infty 4\pi c^2 n a^3 e^{-bc^2} dc$$

$$n = 4\pi n a^3 \int_0^\infty c^2 e^{-bc^2} dc \quad \text{--- (13)}$$

$$\therefore \int_0^\infty c^2 e^{-bc^2} dc = \frac{1}{4} \left(\frac{\pi}{b^3} \right)^{1/2}$$

$$\text{then, } 1 = 4\pi a^3 \frac{1}{4} \left(\frac{\pi}{b^3} \right)^{1/2}$$

$$l = a^3 \left(\frac{\pi}{b}\right)^{3/2}$$

$$a^3 = \left(\frac{b}{\pi}\right)^{3/2} \Rightarrow \left[a = \sqrt[3]{\frac{b}{\pi}}\right] \quad \text{--- (14)}$$

(ii) Value of Constant b :- In order to calculate value of constant b , pressure has to be find in x -direction.

so, pressure working on gas molecule

$$P = \sum_{n=0}^{\infty} 2mv^2$$

total pressure on the gas molecule in x -direction

$$P = \sum_{n=0}^{\infty} 2mv^2 n_v \quad \text{--- (15)}$$

No. of molecules present in v and $vf dv$ range in x -direction:

$$n_v = f(v)dv \times n \quad \{ \text{by eq. (8)} \}$$

$$\therefore f(v) = ae^{-bv^2}$$

$$n_v = nae^{-bv^2} dv$$

on putting value in eq. (15)

$$P = \sum_{n=0}^{\infty} 2mv^2 na e^{-bv^2} dv$$

If distribution of molecules is continuous then Σ can be replace by integration.

$$P = \int_0^{\infty} 2mv^2 na e^{-bv^2} dv$$

$$P = 2mn\alpha \int_0^{\infty} u^2 e^{-bu^2} du$$

$$\therefore \int_0^{\infty} u^2 e^{-bu^2} du = \frac{1}{4} \left(\frac{\pi}{b^3} \right)^{1/2}$$

On putting value

$$P = 2mn\alpha \cdot \frac{1}{4} \left(\frac{\pi}{b^3} \right)^{1/2}$$

$$P = mn \frac{b^{1/2}}{\pi^{1/2}} \cdot \frac{1}{2} \frac{\pi^{1/2}}{b \cdot b^{1/2}} \quad (\because a = \sqrt{\frac{b}{\pi}})$$

$$P = \frac{mn}{2b} \quad \textcircled{16}$$

from the ideal gas equation

$$PV = nRT$$

$$P = \frac{nRT}{V} \quad \textcircled{17}$$

from eq. $\textcircled{16}$ and $\textcircled{17}$

$$\frac{nRT}{V} = \frac{mn}{2b}$$

$$b = \frac{mv}{2RT}$$

$$\therefore \underline{nR} = K \Rightarrow R = \underline{\frac{K}{n}}$$

On putting value

$$b = \frac{mvn}{2kT}$$

Let No. of molecules present in per unit volume is unit. $\{n=1, V=1\}$

M.T.R

$$b = \frac{m}{2kT}$$

(18)

on putting value in eq. (17)

$$a = \sqrt{\frac{m}{2\pi kT}}$$

(19)

Equation (18) and (19) the value of Maxwell's constant.

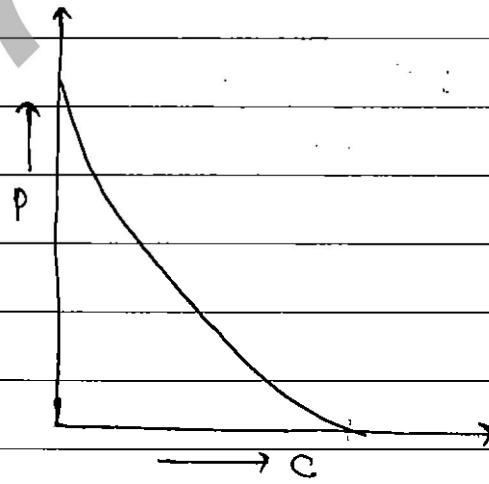
By substituting value in eq. (12) from eq. (18) and (19)
~~****~~

M.T.R

$$dn_c = 4\pi c^2 n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\left(\frac{mc^2}{2kT}\right)} dc \quad (20)$$

Eq. (20) is said to be total solution of Maxwell's distribution law.

Curve between distribution function (P) and velocity of molecule (c): -



- Application of Distribution Function

There are three application of distribution function

(a) Average velocity of gas molecule -

(b) Root mean square velocity of gas molecule

(c) Most probable speed of gas molecule

(a) Average velocity of gas molecule :- We know that from the definition of average -

$$\bar{v} = \frac{\int_0^{\infty} c d n_c}{n} \quad \text{--- (1)}$$

$$\therefore d n_c = 4\pi n a^3 e^{-bc^2} c^2 dc$$

on putting value in eq. (1)

$$\bar{v} = \frac{\int_0^{\infty} 4\pi n a^3 e^{-bc^2} c^2 dc}{n}$$

$$\bar{v} = \frac{4\pi n a^3}{n} \int_0^{\infty} c^3 e^{-bc^2} dc$$

$$\therefore \int_0^{\infty} c^3 e^{-bc^2} dc = \frac{1}{2b^2}$$

then,

$$\bar{v} = 4\pi n a^3 \cdot \frac{1}{2b^2}$$

$$\therefore b = \frac{m}{2Kt}$$

$$\therefore a = \frac{\sqrt{b}}{\sqrt{\pi}} = \sqrt{\frac{m}{2\pi kT}}$$

On putting value, we have

$$\bar{C} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2} \frac{4k^2 T^2}{m^2}$$

$$\bar{C} = 4\pi \frac{m^{3/2}}{2^{3/2} \pi^{3/2} (kT)^{3/2}} \frac{1}{2} \frac{4(kT)^2}{m^2}$$

$$\bar{C} = \frac{16(kT)^{1/2}}{2^{3/2} 2^1 \pi^{1/2} m^{1/2}}$$

$$\bar{C} = \frac{16kT}{\sqrt{2\pi m}}$$

$$\bar{C} = \frac{8kT}{\pi m} \quad \text{--- (2)}$$

(b) Root mean square velocity of gas molecule :-

We know that, from the definition root mean square velocity.

$$C_{r.m.s.}^2 = \frac{\int_0^\infty C^2 dN_C}{n} \quad \text{--- (3)}$$

$$\therefore dN_C = 4\pi n a^3 e^{-bc^2} c^2 dc$$

then,

$$C_{r.m.s.}^2 = \frac{\int_0^\infty 4\pi n a^3 c^4 e^{-bc^2} dc}{n}$$

Dr. K.K. Sharma
9182491592

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9182491592

$$C_{r.m.s}^2 = \frac{4\pi n a^3}{n} \int_0^\infty C^4 e^{-bc^2} dc$$

$$\therefore \int_0^\infty C^4 e^{-bc^2} dc = \frac{3}{8} \left(\frac{\pi}{b^5} \right)^{1/2}$$

then, $C_{r.m.s}^2 = 4\pi n a^3 \cdot \frac{3}{8} \left(\frac{\pi}{b^5} \right)^{1/2}$

$$\therefore b = \frac{m}{2kT}$$

$$a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}}$$

on putting values,

$$C_{r.m.s}^2 = \pi \left(\frac{m}{2\pi kT} \right)^{3/2} \cdot \frac{3}{2} \pi^{1/2} \left(\frac{2kT}{m} \right)^{5/2}$$

$$C_{r.m.s}^2 = \frac{\pi m^{3/2}}{2^{3/2} \pi^{3/2} (kT)^{3/2}} \cdot \frac{3}{2} \pi^{1/2} 2^{1/2} 2^{3/2} \frac{(kT)^{5/2}}{m^{5/2}}$$

~~$$C_{r.m.s}^2 = \frac{3kT}{m}$$~~

$C_{r.m.s}^2 = \frac{3kT}{m}$	— (9)
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- (c) Most Probable speed of gas molecule :- The velocity by which the maximum molecules move in the system is called most probable speed. At most probable speed $C = C_m$ the probability of molecules should be highest.

Most probable speed is denoted by c_m .

We know that, no. of molecule present in c and $c+dc$ range

$$dn_c = 4\pi n a^3 e^{-bc^2} c^2 dc \quad \text{--- (5)}$$

Probability of molecules in the c and $c+dc$ velocity range. $= f(c) dc$

Probability = No. of molecules

No. of molecules present in per unit volume

$$f(c) dc = \frac{dn_c}{n}$$

on putting value from eq (5)

$$f(c) dc = \frac{4\pi n a^3 e^{-bc^2} c^2 dc}{n}$$

$$f(c) = 4\pi a^3 e^{-bc^2} c^2$$

We know that, maximum value of probability is 1. which is constant.

So,

$$f(c) = 4\pi a^3 c^2 e^{-bc^2} = \text{Constant}$$

Dif. with respect to c

$$\frac{df(c)}{dc} = 0 = 4\pi a^3 [2c \cdot 1 \cdot e^{-bc^2} + c^2 e^{-bc^2} (-2bc \cdot 1)]$$

$$0 = 4\pi a^3 2c e^{-bc^2} (1 - bc^2)$$

$$\text{since, } 4\pi a^3 2c e^{-bc^2} \neq 0$$

$$\text{so, } 1 - bc^2 = 0$$

$$1 = bc^2$$

$$C_m = C = \sqrt{\frac{1}{b}}$$

$$\therefore b = \frac{m}{2kT}$$

~~N.T.R.~~

$$C_m = \sqrt{\frac{2kT}{m}}$$

- Maxwell Energy Distribution Function :- Let the mass of gas molecule is m and velocity is c . So the kinetic energy of molecule of gas.

$$E = \frac{1}{2}mc^2 \quad \textcircled{1}$$

$$c^2 = \frac{2E}{m} \quad \textcircled{2}$$

$$\text{Now } E = \frac{1}{2}mc^2$$

Dif. with respect to c

$$\frac{dE}{dc} = \frac{1}{2}m \cdot 2c$$

$$dc = \frac{dE}{mc}$$

$$dc = \frac{dE}{m(2E/m)^{1/2}}$$

By putting value of c^2

$$dc = \frac{dE}{(2mE)^{1/2}} \quad (3)$$

We know that, No. of molecules in E and $E+dc$ velocity range

$\Delta E_c = \text{range}$

$$dn_c = 4\pi n a^3 c^2 e^{-bc^2} dc$$

No. of molecules in E and $E+dc$ energy range

$$dn_E = 4\pi n a^3 \frac{\Delta E}{m} e^{-b \frac{\Delta E}{m}} \frac{dE}{(2mE)^{1/2}} \quad [\text{from (2) and (3)}]$$

$$\therefore b = \frac{m}{2kT} \quad \text{and} \quad a = \sqrt{\frac{m}{2\pi kT}}$$

put the value

$$dn_E = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{\Delta E}{m} e^{-\frac{2E \cdot m}{m \cdot 2kT}} \frac{dE}{(2mE)^{1/2}}$$

$$\boxed{dn_E = \frac{2n E^{1/2} e^{-\frac{E}{kT}} dE}{\pi^{1/2} (kT)^{3/2}}} \quad (4)$$

Equation (4) is called Maxwell's law of energy distribution. "function present in eq. (4) $e^{-E/kT}$ is called Maxwell Boltzmann function."

(i) It is clear from eq. (4) that Maxwell energy distribution function does not depend upon mass of gas molecule it only depends upon transferred energy.

(ii) Probability of molecules in energy E and $E+dc$ range

$$f(E) dE = \frac{dn_E}{n} \quad (5)$$

$$f(E) dE = \frac{2n E^{1/2} e^{-E/kT} dE}{\pi^{1/2} (kT)^{3/2} n}$$

$$f(E) = \frac{2E^{1/2} e^{-E/kT}}{\pi^{1/2} (kT)^{3/2}} \quad \text{--- (6)}$$

We know that maximum value of probability is 1.
which is constant.

From eq. (6)

$$f(E) = \frac{2E^{1/2} e^{-E/kT}}{\pi^{1/2} (kT)^{3/2}} = \text{max.} = \text{Constant} \quad \text{--- (7)}$$

(iii) It is clear from eq. (7) that if energy of molecule of gas is zero ($E=0$) probability of molecules will be zero which valid in classical physics.

(a) Average Energy :- We know that,
from the definition of average.

$$\bar{E} = \frac{\int_0^{\infty} E dn_F}{n}$$

{from eq. (4)}

$$E = \int_0^{\infty} \frac{E 2n E^{1/2} e^{-E/kT} dE}{\pi^{1/2} (kT)^{3/2} n}$$

$$E = \frac{2}{\pi^{1/2} (kT)^{3/2}} \int_0^{\infty} E^{3/2} e^{-E/kT} dE$$

$$\bar{E} = \frac{2}{\pi^{1/2} (kT)^{3/2}} \int_0^{\infty} (E^{1/2})^3 e^{-E/kT} dE$$

Let $E^{1/2} = x \Rightarrow E = x^2$
D.w.r to x
 $dE = 2x dx$

on putting values,

$$\bar{E} = \frac{2}{\pi^{1/2} (kT)^{3/2}} \int_0^{\infty} x^3 e^{-x^2/kT} 2x dx$$

$$\bar{E} = \frac{4}{\pi^{1/2} (kT)^{3/2}} \int_0^{\infty} x^4 e^{-x^2/kT} dx$$

$$\therefore \int_0^{\infty} x^4 e^{-x^2/kT} dx = \frac{3}{8} \left[\frac{\pi}{(1/kT)^5} \right]^{1/2}$$

then,

~~$$\bar{E} = \frac{4}{\pi^{1/2} (kT)^{3/2}} \frac{3 \pi^{1/2} (kT)^{5/2}}{8} (kT)^4$$~~

~~$$\bar{E} = \frac{3}{2} kT$$~~ ⑧

- (b) Most Probable Energy :- The energy with which the maximum molecules accept it in the system is called most probable energy.

from eqn ⑦

$$f(E) = \frac{2E^{1/2} e^{-E/KT}}{\pi^{1/2} (KT)^{3/2}} = \text{max.} = \text{constant}$$

i. with respect to E

$$\frac{df(E)}{dE} = 0 = \frac{2}{\pi^{1/2} (KT)^{3/2}} \left[E^{1/2} \cdot e^{-E/KT} \left(\frac{-1}{KT} \right) + e^{-E/KT} \cdot \frac{1}{2} E^{-1/2} \right]$$

$$0 = \frac{2e^{-E/KT}}{\pi^{1/2} (KT)^{3/2}} \left[\frac{-E^{1/2}}{KT} + \frac{1}{2E^{1/2}} \right]$$

$$\therefore \frac{2e^{-E/KT}}{\pi^{1/2} (KT)^{3/2}} \neq 0$$

$$\frac{-E^{1/2}}{KT} + \frac{1}{2E^{1/2}} = 0$$

$$\frac{E^{1/2}}{KT} = \frac{1}{2E^{1/2}}$$

$$E^{1/2+1/2} = \frac{1}{2} KT$$

$$E_m = E = \frac{1}{2} KT$$

⑨

(c) Probability on the most probable energy / Maximum probability

in putting $E = E_m$ in the ⑧ ⑨ ⑦

$$[f(E_m)]_{\max.} = \frac{2E_m^{1/2} e^{-E_m/kT}}{\pi^{1/2} (kT)^{3/2}} = \text{max.} = \text{constant}$$

$$\therefore E_m = \frac{1}{2} kT$$

Put the value.

$$[f(E_m)]_{\max.} = \frac{2(1/2 kT)^{1/2} e^{-1/2 kT \cdot \frac{1}{kT}}}{\pi^{1/2} (kT)^{3/2} (kT)^1}$$

$$[f(E_m)]_{\max.} = \frac{2^{1/2} e^{-1/2}}{\pi^{1/2} kT}$$

$$[f(E_m)]_{\max.} = \frac{1}{kT} \sqrt{\frac{2}{\pi}}$$

Important Numericals

Q.1 Given $M_H = 2$; $M_N = 28$; $T_N = 40^\circ C = 313K$
 $T_H = ?$; $\bar{C}_H = \bar{C}_N$

Solution We know that, from the average speed

$$\bar{C} = \sqrt{\frac{8kT}{\pi m}}$$

for Hydrogen atom

$$\bar{C}_H = \sqrt{\frac{8kT_H}{\pi M_H}} \quad \text{--- (1)}$$

for Nitrogen molecule

$$\bar{C}_N = \sqrt{\frac{8kT_N}{\pi M_N}} \quad \text{--- (2)}$$

according to question

$$\overline{C_H} = \overline{C_N}$$

$$\sqrt{\frac{8kT_H}{M_H}} = \sqrt{\frac{8kT_N}{M_N}}$$

$$T_H = M_H \cdot \frac{T_N}{M_N}$$

on putting value

$$T_H = 2 \times \frac{313}{28}$$

$$T_H = 22.3 \text{ K}$$

Q.2

$$\text{Given: } k = 1.38 \times 10^{-23} \text{ J/K}$$

$$m = 3.35 \times 10^{-27} \text{ kg}$$

$$T = 27^\circ\text{C} \rightarrow 27 + 273 = 300 \text{ K}$$

$$\text{Gr.m.s} = ?$$

Solution: We know that, root mean square velocity

$$\text{Gr.m.s} = \sqrt{\frac{3kT}{m}}$$

on putting value

$$\text{Gr.m.s} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{3.35 \times 10^{-27}}}$$

*** Q.3**

Given :- $m = 3 \times 10^{-26} \text{ kg}$ $k = 1.38 \times 10^{-23} \text{ J/K}$
 $T = 127^\circ\text{C} = 127 + 273 = 400 \text{ K}$

$$C_m = ?$$

Solution :- We know that, most probable speed

$$C_m = \sqrt{\frac{2kT}{m}}$$

$$C_m = \sqrt{\frac{2 \times 1.38 \times 10^{-23} \times 400}{3 \times 10^{-26}}}$$

$$C_m = \sqrt{\frac{11.04 \times 10^{-23}}{3 \times 10^{-26}}}$$

$$\boxed{C_m = 660 \text{ m/sec.}}$$

Q.4

Given :- Calculate the temperature at which root mean square velocity of any molecule at 100°C becomes double of root mean square velocity?

Solution :- We know that, root mean square velocity

$$C_{rms} = \sqrt{\frac{3kT}{m}}$$

according to question at $100^\circ\text{C} = 373 \text{ K}$

$$\sqrt{\frac{3kT}{m}} = 2 \sqrt{\frac{3k \times 373}{m}}$$

$$\frac{3kT}{m} = \frac{4 \times 3k \times 373}{m}$$

$$T = \cancel{1049} 1492 \quad \Rightarrow \boxed{T = 1492} \text{ Ans}$$

Q.5

Given :- At which temperature root mean square velocity of H atom will become its double at NTP.

We know that, root mean square velocity

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

Let at the T' temperature it becomes double.
then,

$$\sqrt{\frac{3kT'}{m}} = 2 \sqrt{\frac{3kT}{m}}$$

$$\frac{3kT'}{m} = 4 \times \frac{3kT}{m}$$

$$T' = 4 \times T$$

$$T' = 4 \times 273 = 1132 \text{ K}$$

- Degrees of Freedom To define the position and configuration of any particle coordinates are essential.

We know that, position vector of a particle has dependency upon coordinates but coordinates of particle are free variables. "These free variables (coordinates) are called degree of freedom."

i.e. degree of freedom of any particle is defined by free variable (coordinate) of that particle.

If any partical does rectilinear motion (1-dimensional) then its motion is explain by one-coordinate.

Therefore degree of freedom of 1-dimensional motion will be one.

If any partical is in two-dimensional motion then its motion is explain by two coordinates. That's why degree of freedom of 2-D motion will be two.

If a partical is in three-dimensional motion then three coordinates are required to explain its motion. Therefore degree of freedom will be three in 3-D motion.

In the translation motion degree of freedom of a partical is three.

1: Translation motion takes place in monoatomic molecule and we know that for the translation motion degree of freedom is three therefore in the monoatomic molecule degree of freedom is three.

$$\text{ie } \boxed{f = 3} \text{ M.F. } \{ f = \text{degree of freedom}\}$$

2: There is two types of motion is possible in diatomic molecule that's why for the diatomic molecule degree of freedom is 5.

- (a) Translation motion
- (b) Vibrational motion

Where, N = No. of atoms

Date 15/0

k = No. of bonds

We know that degree of freedom is 3 for the translation motion and for the vibrational motion degree of freedom is two.

$$\text{i.e. } f = f_T + f_V$$

$$f = 3 + 2$$

$$f = 5$$

(iii) In the polyatomic molecule there are two types of motion take place.

(a) Translation motion

(b) Rotational motion

In the polyatomic molecule degree of freedom for the translation motion is three and for the rotational motion degree of freedom is three.

Therefore, total degree of freedom in polyatomic molecule is six.

$$f = f_T + f_R$$

$$f = 3 + 3$$

$$f = 6$$

NOTE :- In the classical physics, at the normal temperature above degree of freedom are valid but as increase in temperature no. of free variable also increase therefore degree of freedom also changes.

- Heat Capacity in Classical Physics :- We know that, heat capacity at constant volume

$$C_V = \left(\frac{dQ}{dT} \right)_V \quad \textcircled{1}$$

heat capacity at the constant pressure

$$C_P = \left(\frac{dQ}{dT} \right)_P \quad \textcircled{2}$$

from the first law of thermodynamics

$$dQ = dU + dW$$

$$dQ = dU + PdV \quad \textcircled{3} \quad (\because dW = PdV)$$

for the constant volume

$$V = \text{cont.}$$

$$dV = 0$$

Put the value in eq. $\textcircled{3}$, we have

$$dQ = dU$$

on substituting value in eq. $\textcircled{1}$

$$C_V = \left(\frac{dU}{dT} \right)_V \quad \textcircled{4}$$

for constant pressure:

$$PV = RT$$

Q. with respect to T

$$\therefore nR = Nk$$

$$\frac{PdV}{dT} = R \cdot T$$

$$[PdV = RdT]$$

put the value in eq. $\textcircled{3}$

$$dQ = dU + RdT \quad \textcircled{5}$$

on substituting value in eq. (2) from eq.n (5)

$$C_p = \left[\frac{dU + RdT}{dT} \right]$$

$$C_p = \left(\frac{dU}{dT} \right)_V + R$$

from eq.n (4)

$$C_p = C_V + R \text{ M.R.}$$

$$C_p - C_V = R \quad \text{--- (6)}$$

Equation (6) is called

relation.

$$\gamma = \frac{C_p}{C_V}$$

1 Internal energy of system :-

$$U = f \left(\frac{1}{2} kT \right) \text{ M.R.} \quad \text{--- (1)}$$

here f = degree of freedom

2 Heat Capacity.

(i) heat capacity at constant volume

$$C_V = \left(\frac{dU}{dT} \right)_V$$

$$C_V = \frac{d}{dT} \left[f \left(\frac{1}{2} kT \right) \right]$$

$$C_V = \frac{1}{2} fk \cdot 1$$

$$C_V = \frac{1}{2} R f \quad \text{--- } ②$$

(ii) Heat capacity at constant pressure

We know that from Mayer relation

$$C_P - C_V = R$$

$$C_P = C_V + R$$

from eq. ②

$$C_P = \frac{1}{2} R f + R$$

M.T.R:

$$C_P = \frac{R}{2} (f + 2) \quad \text{--- } ③$$

3: Ratio of Heat Capacity :-

We know that $r = \frac{C_P}{C_V}$

on putting value from eq. ② and ③

$$r = \frac{\frac{R}{2}(f+2)}{\frac{R}{2}f}$$

$$r = 1 + \frac{2}{f} \quad \text{--- } ④$$

(A) For Monoatomic Molecular

We know that degree of freedom for the monoatomic molecule is three.

i.e

$$f = 3$$

(a) Internal Energy

We know that

$$U = f \left(\frac{1}{2} kT \right)$$

$$U = \frac{3}{2} kT$$

$$\therefore f = 3$$

5.

(b) Heat capacity at constant volume

We know that, $C_V = \frac{f}{2} R$ Put the $f = 3$

$$C_V = \frac{3}{2} R$$

(c) Heat capacity at constant pressure

We know that $C_P = \frac{R}{2} (f + s)$ Put the $f = 3$

$$C_P = \frac{5}{2} R$$

(d) Ratio of heat capacity

We know that, $\gamma = 1 + \frac{f}{s}$

$$f = 3$$

$$f = 1 + \frac{2}{3}$$

$$\gamma = \frac{5}{3}$$

(B) For Diatomic Molecular: We know that degree of freedom is 5 for the diatomic molecule.

$$f = 5$$

(a) Internal Energy

We know that $U = f\left(\frac{1}{2}kT\right)$

$$U = \frac{5}{2}kT \quad (f=5)$$

(b) Heat capacity at constant volume

We know that

$$C_V = \frac{1}{2}Rf$$

Put the $f = 5$

$$C_V = \frac{1}{2}R \cdot 5$$

$$C_V = \frac{5}{2}R$$

(c) Heat Capacity at constant pressure

We know that, $C_P = \frac{R}{2}(f+2)$

Put the $f = 5$

$$C_P = \frac{R}{2}(5+2)$$

$$C_P = \frac{7}{2}R$$

(d) Ratio of Heat capacity

We know that $\gamma = 1 + \frac{2}{f}$

$$\gamma = 1 + \frac{2}{5} \quad (f=5)$$

$$\boxed{\gamma = \frac{7}{5}}$$

(e) For Polyatomic Molecule. We know that degree of freedom for the polyatomic molecule is 6 (non-linear).

$$\boxed{f=6}$$

(f) Internal Energy

We know that, $U = f(\frac{5}{2}KT)$

Put the $f=6$

$$U = \frac{6}{2}KT$$

M.T.R

$$\boxed{U = 3KT}$$

(g) Heat capacity at constant volume

We know that, $C_V = \frac{1}{2}Rf$

since $f=6$

$$C_V = \frac{1}{2}R \cdot 6$$

$$\boxed{C_V = 3R}$$

③ Heat capacity at constant Pressure

We know that, $C_p = \frac{R}{2} + C_f + 2$

$$C_p = \frac{R}{2} + C_f + 2 \quad (f = C_v) \quad (C_p = 4R)$$

$$\boxed{C_p = 4R}$$

④ Ratio of Heat capacity

We know that, $r = \frac{C_p}{C_v} = 1 + \frac{2}{f}$

on putting $f = \frac{6}{5}$

$$r = 1 + \frac{2}{\frac{6}{5}} = \frac{4}{3}$$

$$\boxed{r = \frac{4}{3}}$$