

Q.1 State the law of Equipartition of Energy?

⇒ Statement → In ~~totally~~ Thermal equilibrium, the total energy of a gas is equally distributed among all the degrees of freedom. The energy per molecule per degree of freedom is equal to $\frac{1}{2} k_B T$. k_B = Boltzmann constant, T - absolute temp

Expression for average energy of a gas molecule

⇒ Energy of a gas molecule for n degrees of freedom is

$$E = n \left(\frac{1}{2} k_B T \right)$$

For monoatomic gas : $n=3$

$$E = 3 \left(\frac{1}{2} k_B T \right) = \frac{3}{2} k_B T \text{ for 1 molecule}$$

For 1 mole

$$E = \frac{5}{2} k_B T \times 1 \text{ mole} \Rightarrow E = \frac{5}{2} k_B T \cdot N_A$$

$$\boxed{E = \frac{5}{2} RT}$$

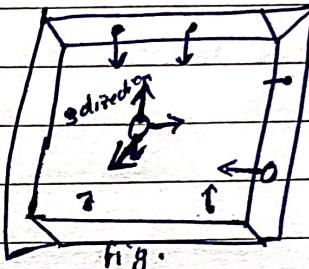


fig.

For triatomic gas : $n=6$

$$E = 6 \left(\frac{1}{2} k_B T \right) = \frac{3}{2} k_B T \text{ for 1 molecule}$$

For 1 mole

$$E = 3 k_B T \times 1 \text{ mole} \Rightarrow E = 3 k_B T \cdot N_A$$

$$\boxed{E = 3RT}$$

Ratio of specific heats : It is the ratio of a gas at constant Pressure (C_P) to the specific heat at constant volume (C_V)

$$\gamma = \frac{C_P}{C_V} \quad \boxed{\gamma = 1 + \frac{2}{n}} \quad n - \text{no of deg of freedom}$$

For monoatomic gas : $n=3$

$$\gamma = 1 + \frac{2}{3} = 1 + \frac{2}{\frac{3}{3}} = 1 + 0.67 \quad \gamma = 1.67 \quad \gamma = 1 + \frac{2}{5} = 1 + 0.4 \quad \gamma = 1.4$$

For triatomic gas : $n=6$

$$\gamma = 1 + \frac{2}{6} = 1 + 0.33 \Rightarrow E \gamma = 1.33 \quad \underline{\text{Proved}}$$

- Q2. Define Entropy. Show that the entropy of a perfect gas remains constant in a reversible process and increases in irreversible process.
- ⇒ Entropy is a thermodynamic state quantity that is a measure of randomness or disorder in the molecule of the system.
- It is represented by S while change in disorder from start to complete is represented by ΔS .

$$\Delta S = [S_{\text{final}} - S_{\text{initial}}]$$

Entropy equation -

$$ds = dq/T \rightarrow ①$$

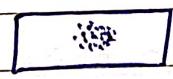
Thermodynamic function such as ΔE , ΔH , ΔS depend only initial and final states of the system but not on the ~~exact~~ path.

- A measurement of the degree of randomness of energy in a system.

- The lower entropy the more ordered and less random.



High disorder (High entropy)



low disorder (low entropy)

⇒ Entropy is maximum Randomness / disorder in Gas.

Gas > liquid > solid → less randomness

Showing → F & He

The thermal property of a body Entropy I

Q3 Entropy & reversible & irreversible process?

Entropy literally means 'transformation'. The concept of entropy was introduced by Clausius in 1854, while working on derivation and application of second law of thermodynamics. The temp of a body remains constant in an isothermal process whereas no heat is added to or taken away from the system in an adiabatic process. When a gas is compressed adiabatically work is done on the gas, hence its heat energy as well as its temperature increases. On the other hand when work is done by the gas, the heat energy as well as temperature decreases. This shows that in an adiabatic process neither the heat energy nor the temperature remains constant. These two increase or decrease together, but there is something which remains constant, just as temp remains constant in isothermal process.

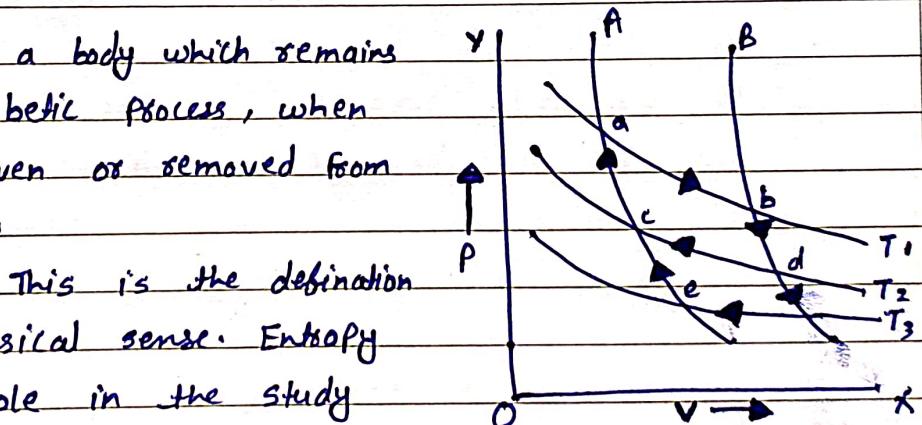
The thermal property of a body which remains constant during an adiabatic process, when no heat energy is given or removed from it is called entropy.

This is the definition

of entropy in the classical sense. Entropy plays a very vital role in the study of thermodynamics.

Consider a number of isothermal T_1, T_2, T_3 etc. drawn at small but equal temperature differences. Draw two adiabatic A and B so that these cut the isothermal T_1 at a and b; T_2 at c and d and T_3 at e and f shown in the fig.

Consider the Carnot cycle abcd. In going from the point a to b certain amount of heat say Q_1 is absorbed at



Q₃ a temp. T₁, in going from du an amount of heat say Q₂, is given out at a temp T₂ then
 → According to Carnot's theorem.

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

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

if we consider the carnot cycle cdfe, an amount of heat Q absorbed at a temp T₂ and Q₃ will be given out at a temp.

then similarly, we have

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$$

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

In general if Q is the quantity of heat absorbed at a temp going from adiabatic A to the adiabatic B, then

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

If the two adiabetics lie very close to each and S_Q is the quantity of heat absorbed at a temp T in going from one adiabatic to the other change in entropy S_S is given by

$$\boxed{S_S = \frac{S_Q}{T}} \quad \underline{\text{Proved}}$$

PG(1)

- Q.4. Deduce Maxwell-Boltzmann distribution law of velocities.
⇒ Let us consider an ideal gas in a vessel of volume V then according to Maxwell-Boltzmann canonical dist. law -

The no. of molecules in i^{th} energy cell

$$n_i = A e^{-\beta E_i} \quad \rightarrow (i)$$

Now, the no. of molecules having energy E_i and having position co-ordinates $x_i^4 + y_i^4 + z_i^4$, $v_x^4 + v_y^4 + v_z^4$ and velocity component $v_x^4 v_x + dv_x$, $v_y^4 v_y + dv_y$ & $v_z^4 v_z + dv_z$ is given by

$$n_i dx dy dz dv_x dv_y dv_z = A e^{-\beta E_i} dx dy dz \quad \rightarrow (ii)$$

$$E_i = \text{Energy of each molecule} = \frac{1}{2} m v^2$$

$$E_i = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \quad \rightarrow (iii)$$

In eqn (2) constant A can be measured by the fact that total no. of molecules are constant and are equal to N .

On integrating eqn (2) over the all available volume and all range of velocities we get -

$$N = \iiint n_i dx dy dz dv_x dv_y dv_z$$

$$= \iiint A e^{-\beta E_i} dx dy dz dv_x dv_y dv_z$$

$$= A \cdot V \iiint e^{-\beta E_i} dv_x dv_y dv_z \quad \{ \text{from eqn } 23 \}$$

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$$\begin{aligned}
 & \text{From eqn (3)} \\
 & \Rightarrow N = AV \iiint e^{-\beta \left[\frac{1}{2} m(v_x^2 + v_y^2 + v_z^2) \right]} dv_x dv_y dv_z \\
 & \Rightarrow N = AV \left(\int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} mv_x^2} dv_x \right) \left(\int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} mv_y^2} dv_y \right) \left(\int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} mv_z^2} dv_z \right) \\
 & \Rightarrow N = AV \left(\sqrt{\frac{2\pi}{m\beta}} \right) \left(\sqrt{\frac{2\pi}{m\beta}} \right) \left(\sqrt{\frac{2\pi}{m\beta}} \right) \\
 & \Rightarrow A = \frac{N}{V} \left(\frac{m\beta}{2\pi} \right)^{3/2} \\
 & \beta = \frac{1}{KT} \\
 & \therefore A = \frac{N}{V} \left(\frac{m \times 1}{2\pi KT} \right)^{3/2}
 \end{aligned}$$

$$\begin{aligned}
 & \text{Standard integral} \\
 & \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \\
 & a = \frac{m\beta}{2} \\
 & \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} mv^2} dv = \sqrt{\frac{\pi \cdot 2}{\beta m}}
 \end{aligned}$$

Putting value of A in eqn (1) we get

$$n_i dv_x dy dz dv_x dy dz = \frac{N}{V} \left(\frac{m}{2\pi KT} \right)^{3/2} e^{-BE_i} dv_x dy dz \xrightarrow{(4)}$$

Now the no. of molecules having velocity co-ordinates in range v_x to $v_x + dv_x$; v_y to $v_y + dv_y$; v_z to $v_z + dv_z$, irrespective to the position of co-ordinates can be measured by integrating eqn (4) w.r.t to position co-ordinates.

i.e.

$$\begin{aligned}
 n_i dv_x dy dz dv_x dy dz &= \frac{N}{V} \left(\frac{m}{2\pi KT} \right)^{3/2 - BE_i} e^{dv_x dy dz} \iiint dx dy dz \\
 &= \frac{N}{V} \left(\frac{m}{2\pi KT} \right)^{3/2} e^{-BE_i} dv_x dy dz \cdot \Delta V
 \end{aligned}$$

$$n_i dv_x dy dz = N \left(\frac{m}{2\pi KT} \right)^{3/2} e^{-\beta \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2)} \cdot \Delta V \xrightarrow{(5)}$$

We can find the number of molecules having velocity component in range v_x to $v_x + dv_x$ irrespective to v_y^2 & v_z^2 by integrating (5) w.r.t to v_y & v_z .

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Q.U. $n_i dv_{xi} = N \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{\beta m v_x^2 dx}{2}} dv_{xi} \int_{-\infty}^{\infty} e^{-\frac{\beta m v_x^2 dy}{2}} dy \int_{-\infty}^{\infty} e^{-\frac{\beta m v_x^2 dz}{2}} dz$

 $\Rightarrow N \cdot \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{\beta m v_x^2 dx}{2}} dv_{xi} \left[\sqrt{\frac{2\pi}{m\beta}} \right] \left[\sqrt{\frac{2\pi}{m\beta}} \right]$
 $\Rightarrow N \cdot \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{\beta m v_x^2 dx}{2}} dv_{xi} \cdot \left(\frac{2\pi kT}{m} \right)$
 $\Rightarrow N \left(\frac{m}{2\pi kT} \right) \left(\frac{m}{2\pi kT} \right)^{3/2} \cdot e^{-\frac{(1-mv_x^2)dx}{2kT}} dv_{xi} \left(\frac{2\pi kT}{m} \right)$

$n_i dv_{xi} = N \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{-mv_x^2 dx}{2kT} dv_{xi}$

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This eqn is called Maxwell distribution law of velocity and it gives the no. of molecules having energy E_1 & x -component of their velocity as dv_{xi} .

The probability that a molecule will have x -component of their velocity in the range v_xe to $v_xe + dv_{xi}$ is given by

$$\text{Eq. - Left hand P}(v_{xi}) dv_{xi} = \frac{n_i dv_{xi}}{N}$$

$$P(v_{xi}) dv_{xi} = \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{-mv_{xi}^2}{2kT} dv_{xi}$$

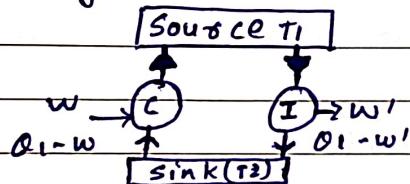
and Probability function $P(v_{xi})$ can be given as

$$P(v_{xi}) = \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{-mv_{xi}^2}{2kT}$$

Proved

- Q5. State and Prove Carnot's theorem. Using 2nd law of thermodynamics
 \Rightarrow It states that "no heat engine working b/w two given temps can be more efficient than the Carnot's reversible heat engine working b/w the same temp."

Proof: In order to prove Carnot's theorem, let us consider a Carnot's heat engine (reversible) C & a (irreversible) heat engine I working b/w same source and sink as shown in the fig.



We have to prove $n_C > n_I$

Let if possible, $n_I > n_C$

where n_I = efficiency of irreversible heat engine

- n_C = efficiency of reversible heat engine

Let engine I absorbs heat Q_1 from source does work w' & rejects $Q_1 - w'$ heat to sink.

\Rightarrow Let engine I works as refrigerator so it absorbe heat $Q_1 - w$ from sink & w work is done on it & it rejects Q_1 heat to the source.

Q5. Also we have assumed

$$\eta_I > \eta_C$$

$$\text{as } w' > w \rightarrow \textcircled{1}$$

$w' - w$ is a positive quantity.

$$\text{Net heat transfer to source} = Q_1 - q_1 = 0$$

$$\text{Net heat absorbed from sink} = (Q_1 - w) - (q_1 - w') \Rightarrow w' - w \rightarrow \textcircled{2}$$

Let us couple 2 engines together then

$$\text{net work done by combined system} = w' - w \rightarrow \textcircled{3}$$

Eq. \textcircled{3} is same as \textcircled{2} which violates second law of thermodynamics. So our assumption

$\eta_I > \eta_C$ is ~~working~~ wrong.

{ same fig and
③ ... ② }

So, we have $\eta_C > \eta_I$. Proved.

Q6. What is black body radiation? State and prove Stefan's law?
 Black body: A perfect black body is one which absorbs totally all the radiations of any wavelength which fall on it. Since it neither reflects nor transmits any radiation it appears black whatever the colour of incident radiation may be. On the other hand when such a body is heated it emits radiations of all possible wavelengths.

Black body radiation: When a black body is placed inside a uniform temp (isothermal) enclosure, it will emit the full radiation of the radiations are independent of the nature of the substance, nature of the walls at the enclosure, and presence of any other body in the enclosure but depends only on temperature. Such radiations in a uniform temperature enclosure are known as black body radiations.

Stefan's Law: It states that the radiation energy E given out by a perfectly black body per second per unit area is directly proportional to the fourth power of the absolute temp i.e.,

$$E = \sigma T^4$$

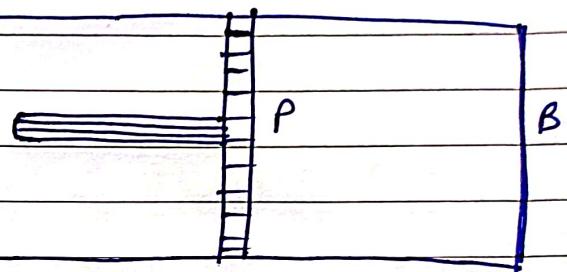
where σ is a constant called Stefan's constant.

If a black body at an absolute temp T_1 is surrounded by another black body at an absolute Temp T_2 . Then the amount of energy E , radiated per unit time per unit area is given by:

$$E = \sigma (T_1^4 - T_2^4)$$

The value of $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$

Q6. Thermodynamic Proof of Stefan's law :- Consider a cylinder of unit area of cross-section having perfectly reflecting walls and the piston P. The base B of the cylinder is perfectly black suppose the cylinder is perfectly black is filled with radiation at uniform temp T. Let a small quantity of radiation $d\Omega$ the incident on the base B from outside due to which the temp rises by an amount dT , which results in the increase of internal energy.



If E is the energy density and v the volume, then Internal energy = VE

\therefore The change in internal energy = $d(VE) = V \cdot dE + E \cdot dv$

If the piston is allowed to move so that the volume increases by a small value dv against a constant pressure P of the radiations inside the cylinder, then from (i) we have

$$\text{External work done} = P \cdot dv = \frac{1}{3} E \cdot dv$$

The energy $d\Omega$ absorbed is partly used in increasing the internal energy and partly in doing the external work.

This change is reversible

$$\begin{aligned}\therefore d\Omega &= (V \cdot dE + E \cdot dv) + \frac{1}{3} E \cdot dv \\ &= V \cdot dE + \frac{4}{3} E \cdot dv\end{aligned}$$

If ds is the change in entropy of radiation, then

$$d\Omega = T \cdot ds$$

$$\text{Hence } T \cdot ds = V \cdot dE + \frac{4}{3} E \cdot dv$$

$$\text{or } ds = \frac{V}{T} dE + \frac{4}{3} \frac{E}{T} \cdot dv \rightarrow (ii)$$

Ques.

Now dS is a perfect differential

$$\therefore dS = \frac{\delta S}{\delta E} dE + \frac{\delta S}{\delta V} dV \rightarrow (iii)$$

Comparing (ii) and (iii), we have

$$\frac{\delta S}{\delta E} = \frac{v}{T} \text{ and } \frac{\delta S}{\delta V} = \frac{4}{3} \frac{E}{ST}$$

$$\therefore \frac{\delta}{\delta V} \left(\frac{\delta S}{\delta E} \right) = \frac{\delta}{\delta E} \left(\frac{\delta S}{\delta V} \right)$$

$$\therefore \frac{\delta}{\delta V} \left(\frac{v}{T} \right) = \frac{\delta}{\delta E} \left(\frac{4E}{3ST} \right) \Rightarrow \therefore \frac{\delta}{\delta V} \left(\frac{v}{T} \right) = \frac{\delta}{\delta E} \left(\frac{4E}{3ST} \right)$$

Now ~~v~~ the temp T is independent of V and is a function of E alone

$$\therefore \frac{1}{T} = \frac{4}{3} \left(\frac{1}{E} - \frac{1}{E^2} \right) \cdot E \frac{ST}{\delta E}$$

$$\Rightarrow \text{or } \frac{1}{T} = \frac{4}{3} \frac{E}{ST} - \frac{4E}{3ST} \cdot \frac{1}{E}$$

$$\text{or } \frac{1}{3} = \frac{4E}{3ST} \cdot \frac{T}{E} \Rightarrow \therefore \frac{\delta E}{E} = \frac{4ST}{T}$$

integrating both sides, we get

$$\log E = 4 \log T + C$$

$$\text{or } E = \sigma T^4$$

where σ is a constant known as Stefan's constant.

Proved

Q.7 Discuss Fermi Dirac distribution law and show that $n_i = \frac{g_i}{[e^{\alpha + \beta E_i}] + 1}$.

⇒ Fermi - Dirac Distribution law: In order to determine the energy (or momentum) distribution of a system of particles obeying F.D. statistics in the most probable or equilibrium state we divide the available volume in the phase space into a large number (say K) of compartments (or quantum states or energy levels) each compartments be marked 1, 2, ..., i, ..., K and their mean energy values be represented by $\epsilon_1, \epsilon_2, \dots, \epsilon_K$ respectively. Let further, we divide each compartment into elementary cells of size h^3 where h is Planck's constant and let them have g_1, g_2, \dots, g_K cells respectively. Let there be $n_1, n_2, \dots, n_i, \dots, n_K$ particles respectively. Let there be $n_1, n_2, \dots, n_i, \dots, n_K$ particles respectively in the energy states or compartments marked 1, 2, ..., i, ..., K then, the total number of particles $n = n_1 + n_2 + \dots + n_i + \dots + n_K$.

Our problem is to find the Fermi - Dirac distribution law i.e., the distribution of n Fermions out of the total of n Fermions in g_i cells of the i^{th} compartment. For this purpose, the basic postulates of Fermi - Dirac statistics are:

Thermodynamical Probability of microstate $(n_1, n_2, n_3, \dots, n_K)$ is given as

$$\omega = g_1 \times g_2 \times \dots \times g_K$$

$$f_1 \quad f_2 \quad f_K$$

$$\omega = \frac{g_1!}{n_1!(g_1-n_1)!} \times \frac{g_2!}{n_2!(g_2-n_2)!} \times \dots \times \frac{g_K!}{n_K!(g_K-n_K)!}$$

$$\Rightarrow \omega = \prod_{i=1}^K \frac{g_i!}{n_i!(g_i-n_i)!}$$

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Q7. Taking log on both side

$$\{ \log n = n \log n - n \}$$

$$\log w = \sum_{i=1}^k \log g_i! + \log n_i! - \log (g_i - n_i)!$$

using Stirling formula

$$\Rightarrow \log w = \sum_{i=1}^k (g_i (\log g_i - g_i) + (n_i \log n_i - n_i) - (g_i - n_i) \log (g_i - n_i) - (g_i - n_i))$$

$$\Rightarrow \log w = \sum_{i=1}^k g_i \log g_i - g_i - n_i \log n_i + n_i - (g_i - n_i) \log (g_i - n_i) + g_i - n_i$$

$$\Rightarrow \log w = \sum_{i=1}^k g_i \log g_i - h_i \log n_i - (g_i - n_i) \log (g_i - n_i)$$

$$\Rightarrow d [\log w] = \sum_{i=1}^k 0 - (n_i (\frac{1}{n_i} d n_i) + \log n_i d n_i) - (g_i - n_i) \frac{1}{g_i - n_i} + \log (g_i - n_i) (0 - d n_i)$$

$$\Rightarrow d [\log w] \leq \sum_{i=1}^k [-d n_i + d n_i \log n_i + d n_i + d n_i \log (g_i - n_i)]$$

$$\Rightarrow d [\log w] = \sum_{i=1}^k [\log (g_i - n_i) - \log n_i] d n_i \rightarrow \textcircled{3}$$

Q8 Mean free path: At a given temp a molecule travels in a straight line before collision with another molecule.

The distance travelled by the molecule before collision is termed free path. The free path for a gas molecule varies from time to time due to collisions.

The mean distance travelled by a molecule between two successive collision is called the mean free path denoted λ .

If l_1, l_2, l_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{l_1 + l_2 + l_3 + \dots}{n} \quad \left\{ \text{for } n \text{ successive collision} \right. \\ \left. \lambda = \frac{l_1 + l_2}{2} \right.$$

$$\Rightarrow \lambda = \frac{\bar{v}}{z_1}$$

where \bar{v} average velocity and z_1 collision no.

$$\lambda = \frac{\bar{v}}{\sqrt{2\pi\sigma^2}\bar{v}N} \Rightarrow \lambda = \frac{1}{\sqrt{2\pi\sigma^2}N} \Rightarrow \lambda \propto \frac{1}{\sqrt{2\pi\sigma^2}P}$$

$$\because N = P/RT \Rightarrow \lambda = \frac{n}{pd} \quad \begin{matrix} n \rightarrow \text{coefficient} \\ d \rightarrow \text{density} \end{matrix}$$



It may be concluded that -

- ① The mean free path is directly proportional to absolute temp $\boxed{\lambda \propto T}$
- ② Mean free path inversely proportional to the pressure of the gas at constant Temp

$$\boxed{\lambda \propto \frac{1}{P}}$$

- ③ mean free path inversely proportional to the density of the gas

$$\boxed{\lambda \propto \frac{1}{n}} \quad n \rightarrow \text{density}$$

(Q9) Gibb's Function is the total energy available in the sys to do useful work is called Gibb's free energy. Gibb's free energy is denoted by G_f and defined the given eqn -

$$G_f = H - TS$$

where - G_f = Gibb's free energy of system
 H = enthalpy
 T = Temp
 S = Entropy

let's consider iso-thermal process occurring at temp T .

we can say that -
 $G_1 = H_1 - TS_1$ [Initial state] $\rightarrow (1)$, $G_2 = H_2 - TS_2$ [Final state] $\rightarrow (2)$

substituting eq (ii) by (1) we get

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1) \Rightarrow \Delta G_f = \Delta H - T\Delta S \rightarrow (3)$$

where ΔG_f = change in Gibb's free energy, ΔH = change in enthalpy

ΔS = change in entropy, T = Temp [const]

Variation of Gibb's free energy with temp & press

we know that free energy eqn From II law of thermodynamic

$$G_f = H - TS \rightarrow (1)$$

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

but enthalpy equation -

$$H = U + PV$$

$$dH = TdS + Vdp - Tds - SdT$$

$$dG_f = Vdp - SdT \rightarrow (3)$$

where - H = enthalpy

U = internal energy

P = pressure

V = volume

This expression give the change in free energy with chan in pres

case I: If temp is kept const $dT = 0$

Substituting the value of H in eqn (1) we get

$$G_f = U + PV - TS \rightarrow (2)$$

From eqn (3) :

$$(dG_f)_T = (Vdp)_T \quad (2) \quad \left(\frac{dG_f}{dp}\right)_T = V \rightarrow (4)$$

complete diff in above eqn

$$dG_f = dU + Pdv + Vdp - Tds - SdT$$

From First law of thermodynamic

$$dU = dv + Pdv$$

$$\text{then } dG_f = dq_r + Vdp - Tds - SdT$$

case II: If pressure is const

$$dp = 0$$

$$\text{from eqn (3)} \quad (dG_f)_P = (-SdT)P$$

$$\left(\frac{\partial G_f}{\partial T}\right)_P = -S$$

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Q10 Electron Gas! Electronic gas (or Fermi gas) metals are very good conductors. The high conductivity of metals is due to the presence of free electrons. The free electrons inside a metallic conductor moves about freely within the metal. They continuously collide with the fixed atoms and thus behave like an electron gas. In other words a metallic solid consists of a set of fixed positive ions immersed in a free electron gas. Since electrons have half integral spin angular momentum in units of $\frac{\hbar}{2n}$ they are Fermi particles (or Fermions) and obey Fermi-Dirac statistics. The electrons in a metal have their energies quantised and being Fermi particles obey Pauli's exclusion principle. Such a system of Fermions confined in a volume is known as Fermi gas. Fermi-Dirac derived an expression for the distribution of energies among the electrons in the electron gas in a metal on the basis of these assumptions.

Ex. A familiar ex of Fermi gas is conduction electron in metals.

Q.11 Derive Planck's law of black body radiation and deduce Wien's distribution law?

$\Rightarrow N = \text{Total number of Planck's resonators}$ and $E = \text{their total energy}$

Then,

Average energy per planck's oscillator is given by $\bar{E} = \frac{E}{N}$

If N_0 is the number of resonators having energy zero.

N_1 is the no. of resonators having energy ϵ .

$$N_1 = N_0 e^{-\epsilon/kT}, N_2 = N_0 e^{-2\epsilon/kT}, N_3 = N_0 e^{-3\epsilon/kT} \dots \text{General form}$$

According to Maxwell's law of molecular motion, the energies $0, \epsilon, 2\epsilon, 3\epsilon, \dots, n\epsilon \dots$ are in the ratio of $1 : e^{-\epsilon/kT} : e^{-2\epsilon/kT} : \dots$

Now if $e^{-\epsilon/kT} = y$, we have

$$\Rightarrow N = N_0 + N_1 + N_2 + \dots + N_\infty + \dots$$

$$\Rightarrow N_0 + N_0 e^{-\epsilon/kT} + N_0 e^{-2\epsilon/kT} + \dots + N_0 e^{-n\epsilon/kT} + \dots$$

$$\Rightarrow N = N_0 [1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \dots + e^{-n\epsilon/kT} + \dots]$$

$$\text{Putting } e^{-\epsilon/kT} = y, \text{ we have } \Rightarrow N = N_0 [1 + y + y^2 + \dots + y^n + \dots]$$

$$N = \frac{N_0}{1-y} \quad [\text{for infinite } G.P. \quad S_n = \frac{a(1-y^n)}{1-y}]$$

The total energy of Planck's resonator will be

$$E = 0 + N_0 \epsilon + N_1 \cdot 2\epsilon + N_2 \cdot 3\epsilon + \dots + N_\infty \cdot n\epsilon + \dots$$

$$\Rightarrow \epsilon N_0 + 2\epsilon N_1 e^{-\epsilon/kT} + 3\epsilon N_2 e^{-2\epsilon/kT} + \dots + n\epsilon N_\infty e^{-n\epsilon/kT} + \dots$$

$$\Rightarrow N_0 \epsilon [e^{-\epsilon/kT} + 2e^{-2\epsilon/kT} + 3e^{-3\epsilon/kT} + \dots]$$

$$E = N_0 \epsilon \frac{y}{(1-y)^2} \quad \left| \begin{array}{l} \text{for } G.P. \quad S_n = \frac{a(1-y^n)}{1-y} \\ \qquad \qquad \qquad = \frac{a}{1-y} \end{array} \right. \quad 3x+2x^2+3x^2+\dots$$

Therefore the average energy of a resonator will be $\frac{\epsilon}{(1-y)^2}$

(PQ) ②

$$\textcircled{Q11} \quad \bar{\epsilon} = \frac{\epsilon}{N} = \frac{\text{No. of oscillators} \cdot \epsilon}{(1-\gamma)^2} \Rightarrow \frac{\epsilon \gamma}{(1-\gamma)} = \frac{\epsilon e^{-\epsilon/kT}}{1-e^{-\epsilon/kT}} = \frac{\epsilon}{e^{\epsilon/kT}-1}$$

number of oscillators would be equal to that derived in Q12
from distribution function

According to Planck's hypothesis of quantum theory, $\epsilon = h\nu$; $\nu \rightarrow \text{frequency}$

$$\text{Now, } \bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT}-1}$$

Therefore, the energy density belonging to the range $d\nu$ can be obtained by multiplying the average energy of Planck's oscillators by the no. of oscillators per unit volume, in this frequency range $\nu \in (\nu_1 + d\nu)$.

$$\Rightarrow \text{i.e., } E\nu d\nu = \left(\frac{8\pi\nu^2}{c^3} \right) \left(\frac{h\nu}{e^{h\nu/kT}-1} \right)$$

$$E\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT}-1} d\nu$$

where $E\nu d\nu$ - energy density (i.e. total energy per unit vol.) belonging to the range $d\nu$. This eqn is called [Planck's radiation law].

The energy density $\epsilon \lambda d\lambda$ belonging to range $d\lambda$ can be obtained by using the relation $\nu = \frac{c}{\lambda}$, hence $d\nu = \frac{c}{\lambda^2} d\lambda$.

$$\text{Hence, } \nu = \frac{c}{\lambda}, \text{ hence } d\nu = \frac{c}{\lambda^2} d\lambda$$

$$\text{we get, } \epsilon \lambda d\lambda = \frac{8\pi h}{c^3} \left(\frac{c^3}{\lambda^3} \right) \cdot \frac{1}{e^{hc/\lambda kT}-1}$$

$$E \lambda d\lambda = \frac{8\pi hc}{c^5} \frac{d\lambda}{e^{hc/\lambda kT}-1}$$

This is Planck's radiation law in terms of wavelength.

Note: No. of mode of vibration per unit volume of ν & No. of oscillators per unit volume = 2

$$= \frac{8\pi \nu^2 d\nu}{c^3}$$

Power

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(Q2) Weins distribution law using Planck's law.

⇒ Planck's law is

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

when wavelength are short

$$e^{hc/\lambda kT} \gg 1$$

$$\therefore e^{hc/\lambda kT} - 1 \approx e^{hc/\lambda kT}$$

Hence

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT}}$$

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda$$

$$\text{Let } 8\pi hc = A \quad \text{and} \quad \frac{hc}{k} = B$$

$$u(\lambda)d\lambda = Ah^{-5} e^{-B/\lambda T} d\lambda$$

Proved.

Q.12 Deduce Maxwell Boltzmann law?

⇒ Stat: Distribute energy in identical but distinguishable particles / to prove: $n_i = \frac{g_i}{e^{\alpha} + \beta E_i}$

Proof: Let n_1, n_2, \dots, n_K represent no. of molecules in the energy intervals 1, 2, 3, ..., K with the mean energies E_1, E_2, \dots, E_K

$$\therefore n = n_1 + n_2 + \dots + n_K = \sum_{i=1}^K n_i$$

$$\therefore n = n_1 + n_2 + \dots + n_K = \sum_{i=1}^K = 0 \rightarrow \textcircled{I}$$

$$\text{Again } E = n_1 E_1 + n_2 E_2 + \dots = \sum_{i=1}^K n_i E_i$$

$$\therefore E \text{ is constant, } dE = \sum dn_i; \sum_{i=1}^K = 0 \rightarrow \textcircled{II}$$

(eqn \textcircled{I} \times \alpha) + (eqn \textcircled{II} \times \beta) we get

$$\alpha dn_i + \beta dE = 0 \rightarrow \textcircled{III}$$

$$\text{Now, } W = n! \prod \frac{(g_i)^{n_i}}{n_i!}$$

Taking log on both sides

$$\ln W = \ln(n!) + \sum n_i \ln g_i - \sum \ln n_i!$$

Stirling's form $\ln n! = n \ln n - n$ $\ln W =$

$$n \ln n - n + \sum n_i \ln g_i - \sum \ln n_i$$

$$\ln W = n \ln n + \sum n_i \ln g_i - \sum \ln n_i$$

$$\therefore d(\ln W) = 0$$

$$\therefore 0 = 0 + \sum dn_i \ln g_i - \sum dn_i \ln n_i$$

$$\sum_{i=1}^K (\ln g_i - \ln n_i) dn_i = 0 \rightarrow \textcircled{IV}$$

Comparing 3 & \textcircled{IV}

$$\ln \frac{g_i}{n_i} = \alpha + \beta E_i, g_i = n_i e^{\alpha + \beta E_i}$$

$$\boxed{n_i = \frac{g_i}{e^{\alpha} + \beta E_i}}$$

Proved

Teacher's Signature : _____

Q13 Deduce Bose-Einstein distribution law:

$$\Rightarrow n_i = \frac{g_i}{e^{\beta E_i} - 1}$$

= Let in a system there are total n particles and K compartments and are distributed in g_i cells.

$$\Rightarrow \text{Total no of particles } n = n_1 + n_2 + \dots + n_K$$

$\therefore n_i$ particles are now distributed in g_i cells in a way-

$$w_i = \frac{g_i^{n_i} (n_i + g_i - 1)!}{n_i! g_i!} \Rightarrow w_i = \frac{g_i^{n_i} (n_i + g_i - 1)!}{n_i! g_i^{n_i}}$$

$$w_i = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

Total thermodynamic probability

$$w = \prod_{i=1}^K \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \approx \frac{(n_i + g_i)!}{n_i! g_i!} \quad n_i + g_i \gg 1, g_i$$

$$\therefore w = \frac{(n_i + g_i)!}{n_i! g_i!} \quad \text{Taking log on both sides}$$

$$\ln w = \ln (n_i + g_i)! - \ln n_i! - \ln g_i!$$

According to Stirling's formula

$$\Rightarrow \ln n! = n \ln n - n$$

$$\Rightarrow \ln w = (n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - n_i + g_i \ln g_i + g_i$$

At maximum w , $d(\ln w) = 0$

$$\Rightarrow d(\ln w) = \ln (n_i + g_i) dn_i + (n_i + g_i) \frac{dn_i}{n_i + g_i} - \ln n_i dn_i - \ln n_i dn_i - n_i \frac{dn_i}{n_i} + dn_i - dn_i \cancel{d(\ln w)}$$

$$\Rightarrow d(\ln w) = \ln (n_i + g_i) dn_i + dn_i - \ln n_i dn_i - dn_i$$

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$$\text{Q3.} \Rightarrow d(\ln \omega) = \ln(n_i g_i) d n_i - \ln n_i d n;$$

$$\Rightarrow d(\ln \omega) = \varepsilon \left[\ln \frac{n_i g_i}{n_i} \right] d n_i$$

$$\varepsilon \left[\ln \frac{n_i g_i}{n_i} \right] d n_i = 0 \rightarrow \textcircled{1}$$

from eqn (1) \downarrow

$n = \text{constant}$

$$\varepsilon d n_i = 0 \rightarrow \textcircled{2}$$

$E = \text{constant}$

$$\varepsilon d n_i \varepsilon_i = 0 \rightarrow \textcircled{3}$$

$$\text{eq } \textcircled{2} \times \alpha + \textcircled{3} \times \beta$$

$$\alpha [d n_i + \beta \varepsilon d n_i \varepsilon_i] = 0 \rightarrow \textcircled{4}$$

(i) $\alpha \textcircled{4}$ compare

$$\varepsilon \left[\ln \frac{n_i g_i}{n_i} \right] d n_i = \varepsilon [\alpha + \beta \varepsilon_i] d n_i \left[\ln \frac{n_i g_i}{n_i} - \alpha - \beta \varepsilon_i \right] d n_i = 0$$

$$\Rightarrow \ln \frac{n_i g_i}{n_i} = \alpha + \beta \varepsilon_i$$

$$\Rightarrow \frac{n_i g_i}{n_i} = e^\alpha + \beta \varepsilon_i \quad , \quad \frac{1+g_i}{n_i} = e^\alpha + \beta \varepsilon_i$$

$$\Rightarrow \frac{g_i}{n_i} = e^\alpha + \beta \varepsilon_i - 1$$

$$\Rightarrow \frac{n_i}{g_i} = \frac{1}{e^\alpha + \beta \varepsilon_i - 1}$$

$$\Rightarrow n_i = \frac{g_i}{e^\alpha + \beta \varepsilon_i - 1} \quad \underline{\text{Proved}}$$

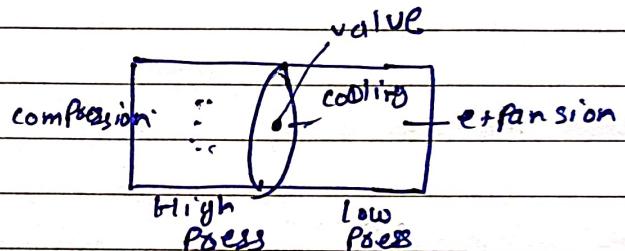
0.14 Joule - Thompson effect .

→ The Joule Thompson effect is a thermodynamic process that occurs when a fluid (gas) expands from high press to low press at constant enthalpy (an isenthalpic process)

Principle for liquefaction of gases. Gases are liquified applying J. H. effect.

when the highly compressed gas is suddenly allowed to expand it causes cooling

$$dH = \left[\frac{\partial H}{\partial T} \right]_P dT + \left[\frac{\partial H}{\partial P} \right]_T dP$$



Joule Thompson coefficient

high
press low
press

→ The Joule Thompson coefficient is a measure of the change in temp with press during a const enthalpy process. denoted by μ_{JT}

$$M_{JT} = \frac{\partial T}{\partial P}$$

if $\mu_{ST} < 0$ temp. increase

$MJT = 0$ temp remain const

$\Delta T > 0$ temp decrease

If the gas temp is - ,

Below the inversion temp

Then $-M_{JT}$ = positive

$\therefore \partial P$ = always negative

∂T = negative

gas = cool

If gas temp is

Above the inverse tan

then, $\Delta S_T = \text{Negative}$

∇P = Always negative

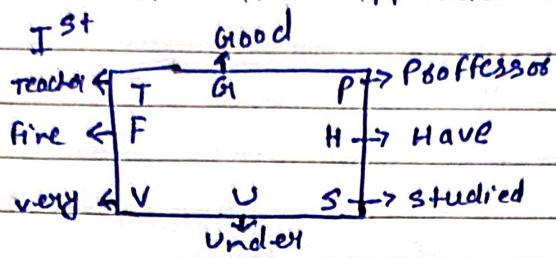
$\delta T = \text{Positive.}$

Teacher's Signature :

Powered

Q15 Maxwell's relation and application:

⇒ Relation 1st



Good Professor Have studied under very fine Teacher

Relation 1.

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \left. \begin{array}{l} \{ S \& P \text{ come together} \\ \{ \text{written on both} \\ \text{side} \end{array} \right.$$

Relation 2.

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad \left. \begin{array}{l} \{ \text{No need of } (\text{)} \text{ when} \\ \text{both are not at} \\ \text{same time} \end{array} \right.$$

Relation 3.

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad \left. \begin{array}{l} \{ \text{no need of } (\text{)} \text{ when} \\ \text{both } S \& P \text{ not} \\ \text{at same time} \end{array} \right.$$

Relation 4.

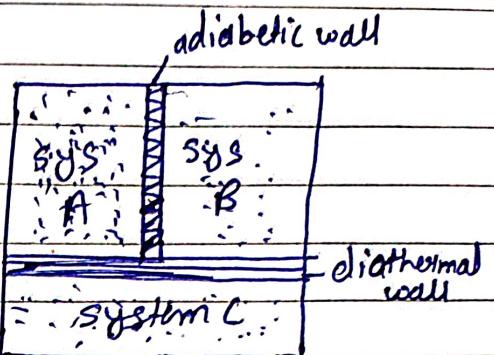
$$\left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T \quad \left. \begin{array}{l} \{ S \& P \text{ come together} \\ \{ \text{written on both} \\ \text{side} \end{array} \right.$$

Proved

Q.16 zeroth law of thermodynamics:

⇒ If two thermodynamics system separated with another system if they have same temp then it is said to be that they are in thermal equilibrium state.

From Fig ① let A, B and C are three systems, system adiabatic wall (which does not allow heat to flow) and System C they are separated by diathermic wall (which allow exchange of heat).



If System A and C are in thermal constant:

$$\therefore T_A = T_C \rightarrow ①$$

If system B to C are in thermal contact

$$\therefore T_B = T_C \rightarrow ②$$

From eq ① & ②

$$T_A = T_B \rightarrow ③$$

Therefore we can say System A, B and C are in thermal equilibrium state.

Proved

A17: Third law of Thermodynamics:

At absolute 0 temp the entropy will be zero and the system molecules of the substance or a system are in perfectly ordered. This is the third law of Thermodynamics.

If an object reaches to the absolute 0 temp $0\text{ K} = -273.15^\circ\text{C}$ the atom will stop moving and there will be lowest possible temp change and the molecular motions of the substance becomes zero.

e.g. Hydrogen gas freezes just a few degrees above the absolute 0° temp.

All the substances solidify at temp or higher than 0° temp.

Helium is the only element that can not solidify and remains liquid form at absolute 0° temp.