of Thermodynamics

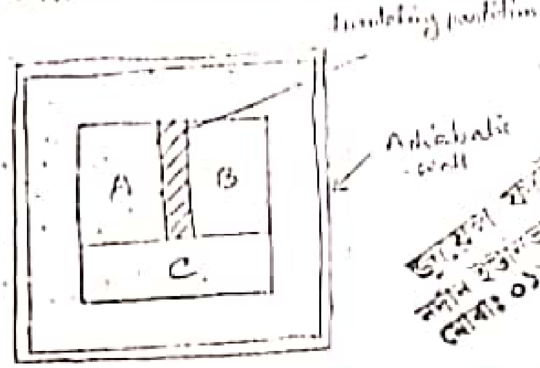
'09, '07, '05, '02

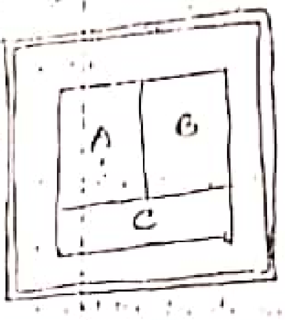
1st class test

separately

i) Zeroth law of Thermodynamics :- If two systems in thermal equilibrium with a third are also in thermal equilibrium with each other.

Explanation: We consider two systems A and B insulated from each other but in good thermal contact with a common system C. Systems A and B will attain thermal equilibrium with third system C.





Now if the insulating partition is removed and systems A and B are brought into thermal contact, we find that there is no further change. This means that the systems A and B are also in thermal equilibrium with another. This is known as zeroth law of thermodynamics.

'09

ii) 1st law of thermodynamics :- states that the amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done.

For a very small change in the state of the system, the law is expressed in the differential form as

$$\delta Q = dU + \delta W$$

(or) $\partial Q = du + \partial w$

where δQ and δW are not perfect differentials but dU is a perfect differential because U is a function of the state of the system.

6 / 04 / 02 2016

Applications of First law of Thermodynamics

The internal energy of a system is a single valued function of the state variables viz. pressure, volume, temperature etc. In the case of gas, any two of the variables P, V, T are sufficient to define completely its state. If V and T are chosen as the independen variables,

$$U = f(V,T) \quad \ldots\ldots ①$$

$u = f(v,T)$

$u = f(T)$

Differentiating equation ①

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \ldots\ldots ②$$

If an amount of heat δQ is supplied to a thermodynamical system, say an ideal gas and if the volume increases by dV at constant pressure P then according to the first law of Thermodyn

$$\boxed{\delta Q = dU + \delta W} \qquad dQ = dv + dw$$

Here: $\delta W = P.dV$

$$\therefore \delta Q = dU + PdV \quad \ldots\ldots ③$$

Substituting the value of dU from equation ②

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV$$

Dividing both sides by dT

$$\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + P\frac{dV}{dT} \quad \ldots\ldots ④$$

$$\text{or, } \left(\frac{\delta Q}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{dV}{dT} \quad \ldots\ldots ④$$

If the gas is heated at constant volume

$$\left(\frac{\delta Q}{\partial T}\right)_V = C_V \quad \text{and} \quad \frac{dV}{dT} = 0$$

$$\therefore \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

diabatic Equation of a Perfect gas: 2016 2016

Consider 1 gram of the working substance perfectly insulated from the surrounding. If the external work done is dW and the change in internal energy is dU.) then according to the first law of thermodynamics.

$$dQ = dU + dW$$

$$\therefore dQ = dU + PdV \quad \text{.......} ①$$

here P is the pressure of the gas and dV is the change in Volume.

For an adiabatic process, $dQ = 0$

$$dU + PdV = 0 \quad \text{.......} (ii)$$

As the external work is done by the gas at the cost of its internal energy, there is fall in temperature by dT.

$$\boxed{dU = C_v dT} \quad \text{.......} (iii)$$

For an ideal gas, $PV = RT$.

Differentiating the above equation, we have.

$$PdV + VdP = RdT$$

$$\Rightarrow dT = \frac{PdV + VdP}{R} \quad \text{.......} (iv)$$

Substituting the value of dT in equation (ii)

$$C_v\left(\frac{PdV + VdP}{R}\right) + PdV = 0$$

$$\Rightarrow C_v\,[PdV + VdP] + RPdV = 0$$

But, $C_p - C_v = R$, Then:

$$\therefore C_v\,[PdV + VdP] + (C_p - C_v)\,PdV = 0$$

$$\therefore C_v VdP + C_p PdV = 0$$

Dividing by $C_v PV$

$$\frac{dP}{P} + \left(\frac{C_p}{C_v}\right)\frac{dV}{V} = 0$$

7 2016

Isothermal process: conv The system in which the system is perfectly eda conducting to the surroundings, and temperat remains constant throughout the process is called isotherm process. During the process the temperature of the workin substance remains constant. It can absorb heat from and given heat to the surround.

$PV = RT$

07

Adiabatic process: The process in which the system is perfectly insulated from the surroundings it can nigther give nor take heal from surroundings is called adiab process. All along the process there is change in tempe hen the gas is heated at constant pressure.

$$\left(\frac{\delta Q}{dT}\right) = C_p$$

∴ From equation (IV)

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore C_p = C_v + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{or, } C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

From Joules experiment, for an ideal gas on oppening the stopcoc no work was done and no heat transfer took place. So. $\delta Q =$ Therefore $dU = 0$. Even though the volume changed, while the tempera is constant, there is no change in the internal energy.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0.$$

From the ideal gas equation,

$$PV = RT.$$

$$\text{or. } P\left(\frac{\partial V}{\partial T}\right)_P = R.$$

$$\therefore C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{But, } \left(\frac{\partial U}{\partial V}\right)_T = 0.$$

$$\therefore C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore C_p - C_V = R.$$

The formula is Known as Mayer's relation.

Here Cp. Cv and R are expressed in the same unit.

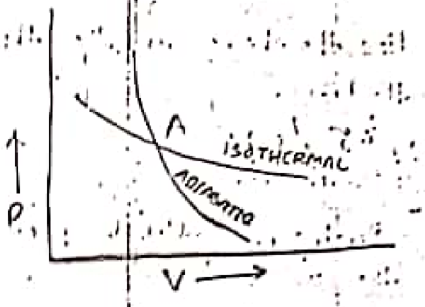
of Adiabatic and isothermal :

In an isothermal process

$$PV = \text{constant}$$

Differentiating, $\therefore PdV + VdP = 0$

$$\therefore \frac{dP}{dV} = -\frac{P}{V}$$



In an adiabatic process.

$$PV^{\gamma} = \text{constant}$$

Differentiating.

$$P\gamma V^{\gamma-1} dV + V^{\gamma} dP = 0$$

$$\therefore \frac{dP}{dV} = -\gamma \frac{P}{V}$$

Therefore, the slope $\left(\frac{dP}{dV}\right)$ of an adiabatic is γ times the slope of the isothermal.

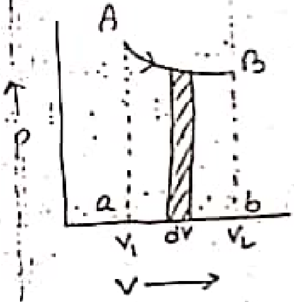
Hence, the adiabatic curve is steeper than the isothermal curve at a point A where the two types curves intersect each other.

04 Work done during an Isothermal Adiabatic Process:

When a gas is allowed to expand isothermally work is done by it. Let the initial and final volumes be V_1 and V_2 respectively.

$$\text{Work done}, \quad W = \int_{V_1}^{V_2} PdV$$

$$= \text{Area } ABba$$



Considering one gram molecule of the gas,

$$PV = RT$$

$$\text{or, } P = \frac{RT}{V}$$

$$\therefore W = RT\int \frac{dV}{V} = RT \ln \frac{V_2}{V_1}$$

$$\therefore W = RT \times 2.303 \log_{10} \frac{V_2}{V_1}$$

$$\therefore \frac{dP}{P} + \gamma \frac{dV}{V} = 0 \quad \left[\because \frac{C_P}{C_V} = \gamma\right]$$

Integrating both sides

$$\therefore \log P + \gamma \log V = \text{constant}$$

or, $\log PV^{\gamma} = \text{constant}$

$$\therefore \boxed{PV^{\gamma} = \text{constant}}$$

This is the relation between pressure and volume during an adiabatic process and is known as Poissons Law.

Taking $PV = RT$

or, $\therefore P = \frac{RT}{V}$

$$\therefore \left(\frac{RT}{V}\right) V^{\gamma} = \text{constant}$$

But. R is constant

$$RTV^{\gamma-1} = \text{constant}$$

$$\boxed{\therefore TV^{\gamma-1} = \text{constant}}$$

Also. $V = \frac{RT}{P}$

$$P\left[\frac{RT}{P}\right]^{\gamma} = \text{constant}$$

or, $\frac{R^{\gamma}T^{\gamma}}{P^{\gamma-1}} = \text{constant}$

or, $\frac{P^{\gamma-1}}{T^{\gamma}} = \text{constant}$

$$\therefore TP^{\frac{1-\gamma}{\gamma}} = \text{constant}$$

$$\left(\frac{P_1}{T_1}\right)^{\frac{1-\gamma}{\gamma}} = \left(\frac{P_2}{T_2}\right)^{\frac{1-\gamma}{\gamma}}$$

$$T_1 P_1^{\frac{1-\gamma}{\gamma}} = (T_2 P_2)^{\frac{1}{\gamma}-1}$$

$$\frac{P^{\gamma-1}}{T_1^{\gamma}} = P_2^{\gamma-1}$$

∴ Resultant pressure, $P = P + p = \left(P + \frac{a}{V^2}\right)$

where P is observed pressure

Correction for Volume:

Due to the finite size of gas molecules, the actual space available for the movement of the molecules is less than the volume of the container.

Let the radius of the molecule is r.

than the volume of the molecule, $x = \frac{4}{3}\pi r^3$

The centre of any two molecules can approach each other only by a minimum distance of 2r.

The volume of sphere of influence of each molecule.

$$s = \frac{4}{3}\pi (2r)^3 = 8 \times \frac{4}{3}\pi r^3 = 8x$$

Let the volume of a container be V.

The volume avaiable for the first molecule = V

The volume available for the second molecule = V − S

The volume available for the nth molecule = V − (n−1) S

∴ The volume available for each molecule.

e avarage space available for each molecule

$$= \frac{V + (V - S) + (V - 2S) + \cdots + [V - (n-1)S]}{n}$$

$$= \frac{n \cdot V}{n} - \frac{S}{n}\{1 + 2 + 3 + \cdots + (n-1)\}$$

$\frac{n(n-1)}{2}$

n der Waals Equation of State

While deriving the perfect gas equation $PV = RT$ on the basis of Kinetic theory, it was assumed that

i) The size of the gas molecule is negligible.

ii) The force of intermolecular attraction is negligible.

But in actual practice, at high pressure the size of the molecule of the gas becomes significant and can not be neglected in comparison with the volume of the gas. Also at high pressure the molecules come closer and the forces of molecular attraction are appreciable.

① **Correction for Pressure**: A molecule in the interior of gas, experiences force of attraction in all directions. and the resultant cohesive force is zero. A molecule near the walls of the container, experience a resultant force inwards. Due to this reason that observed pressure of a gas is less than the ~~observed~~ actual pressure. The correction for pressure p depends on.

① The number of molecules striking a unit area per unit time of the walls of the container and

ⓘⓘ The number of molecule present in a gas give volume.

$p \propto \rho^2$ and ~~ρ~~ $p \propto \frac{1}{V^2}$

or $p = \frac{a}{V^2}$

Here a is a constant and V is the volume of the gas.

Also, $P_1V_1 = P_2V_2$

$$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore W = RT \times 2.303 \log_{10} \frac{P_1}{P_2}$$

Here. the change in the thermal energy of the system is zero. So, the heat can absorbed. by the system is equal do the work done by it

'09, '05, '04

Q.T. (B) Work done during an Adiabatic process.

During an adiabatic process. the system is thermally insulated from the surroundings.

$$W = \int_{V_1}^{V_2} P\,dV = \text{Area } ABba$$

During an adiabatic process. $PV^{\gamma} = \text{constant} = K$.

$$P = \frac{K}{V^{\gamma}}$$

$$\therefore W = K\int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

$$= \frac{K}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right]$$

Since A and B lie on the same adiabatic. $P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$.

$$W = \frac{1}{1-\gamma}\left[\frac{K}{V_2^{\gamma-1}} - \frac{K}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right] \quad \text{......} ①$$

Taking T_1 and T_2 as the temperature at points A and B respectively and considering 1 gm molecule of the gas.

$$P_1V_1 = RT_1 \quad \text{and} \quad P_2V_2 = RT_2$$

Substituting the values in equation①.

$$W = \frac{1}{1-\gamma}\left[RT_2 - RT_1\right]$$

$$\therefore W = \frac{R}{1-\gamma}\left[T_2 - T_1\right].$$

Thus, the work done along any adiabatic between two isot independent of the particular adiabatic

[illegible]

.05 [illegible]

Critical Constants: (T_c, P_c : V_c)

① Critical temperature: It is defined as the maxim temperature at which a gas can be liquefied by the increase of pressure alone. Above this temperature, the gas can not be liquefied how so ever large the applied pressure may be.

② Critical pressure: The pressure necessary to liquefy a gas of at critical temperature is callec the critical pressure.

③ Critical volume: It is the volume which unit mass of a gas occupies at the critical temperat and critical pressure.

④ Critical point: It is that point of on the isothermal for the critical temperature for the critical temperature at which the change of state from the gaseous state to the liquid state takes place under constant values of P_c and V_c.

N.B. These three quantities T_c, P_c and V_c are called critical constants of a gas.

The critical temperature and the correspon value of pressure and volume at the critical poi re called critical constants

$$= V - \frac{s}{n} \cdot \frac{n(n-1)}{2}$$

$$= V - \frac{ns}{2} - \frac{s}{2}$$

As the number of molecules is very large $\frac{s}{2}$ can be neglected.

∴ Average space available of each molecule

$$= V - \frac{ns}{2}$$

$$= V - \frac{n(8x)}{2}$$

$$= V - 4nx$$

$$= V - b$$

where, $b = 4(nx)$ = four times the actual volume of molecules.

Thus the corrected gas equation is.

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

where a and b are Vander walls constant.

This equation is called vander walls equation.

Work done from D to A (Adiabatic process)

$$W_4 = \int_{V_4}^{V_1} P\,dV = -\frac{KR(T_1 - T_2)}{\gamma - 1} = \text{area DFEA}$$

Total work done, $W = W_1 + W_2 + W_3 + W_4$

$$= RT_1 \log\frac{V_2}{V_1} + \frac{K[T_1 - T_2]}{\gamma-1} - RT_2 \log\frac{V_3}{V_4} - \frac{K[T_1 - T_2]}{\gamma - 1}$$

$$= RT_1 \log\frac{V_2}{V_1} - RT_2 \log\frac{V_3}{V_4} \quad \cdots\cdots ①$$

The point A and D are on the same adiabatic.

$$\therefore T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\therefore \frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \quad \text{(ii)}$$

The point B and C are on the same adiabatic

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\therefore \frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \quad ---- \text{(iii)}$$

From equ^n (ii) and (iii)

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

or, $\dfrac{V_1}{V_4} = \dfrac{V_2}{V_3}$

$$\therefore \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substitution in equ^n ①, we get.

Total work done, $W = RT_1 \log\frac{V_2}{V_1} - RT_2 \log\frac{V_2}{V_1}$

$$= R(T_1 - T_2)\log\frac{V_2}{V_1}$$

$$\therefore W = H_1 - H_2 = Q_1 - Q_2.$$

'07, '06, '04, '03

Application of Second law of Thermodynamics:

Work done by the engine per cycle

Carnot's cycle: In order to obtain a continuous supply of work, the working substance is subjected to the following cycle of quasi-static operations known as Carnot's cycle

① Plane the engine containing the working substance over the source at a temperature T_1

Work done from A to B (isothermal process)

$$W_1 = \int_{V_1}^{V_2} P\,dV = RT_1 \log \frac{V_2}{V_1} = \text{area } ABGE \qquad [PV = RT$$

(ii) Work done from B to C (Adiabatic process)

$$W_2 = \int_{V_2}^{V_3} P\,dV = RK \int_{V_2}^{V_3} \frac{dV}{V^{\gamma}} = RK \left[\frac{V^{\gamma-1}}{\gamma-1} \right]_{V_2}^{V_3} \qquad [PV^{\gamma} = K$$

$$= \frac{KR(T_1 - T_2)}{\gamma - 1} = \text{area } BCHG$$

(iii) Work done from C to D (isothermal process)

$$W_3 = \int_{V_3}^{V_4} P\,dV = RT_2 \log \frac{V_4}{V_3}$$

$$= -RT_2 \log \frac{V_3}{V_4} = \text{area } CHFD$$

ersible process. A process is said to be reversible if it can be retracted back exactly in the opposite direction so that the working substance passes exactly in the same state in all respect as in the case of direct process.

In a reversible process there is no loss of heat due to friction or otherwis

Irreversible process: An irreversible process is one which can not be retracted in opposite direction by changing the external conditions infinitesimally.

09, 08, 03

Second law of Thermodynamics:

1st part: It is impasible to get continuous supply of work from a body by cooling it to a temperature lower than that of its surroundings. (Lord Kelvin's statement).

2nd part: It is imposible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing any external work on the substance.

Planck's statement: It is imposible to construct an engine which. working in a complete cycle. will produce no effect other than the raising of a weight and the cooling of a heat reservoir.

Kalvin. Planck statement: It is imposible to construct engine which. operating in a cycle. has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work.

Clausius Statement: It is imposible for a self-acting machine working in a cycle process. unaided by external agency to transfer heat from a body at a lower temerature to a body at a higher temperature.

From one adiabatic to other adiabatic heat energy is either absorbed or rejected. The quantity of heat absorbed or rejected is not constant but it depends upon the higher temp. and the temp. more in the heat energy absorbed or rejected is and vice versa. The quantity H/T between two adiabatics is constant and this is called the change in entrophy. Let the entropy for the adiabatics L and M be S_1 and S_2 respectively

$$\therefore S_2 - S_1 = \frac{H}{T} = \text{constant}$$

If the adiabatics are very close, and the heat absorbed or rejected is δH at a temp. T,

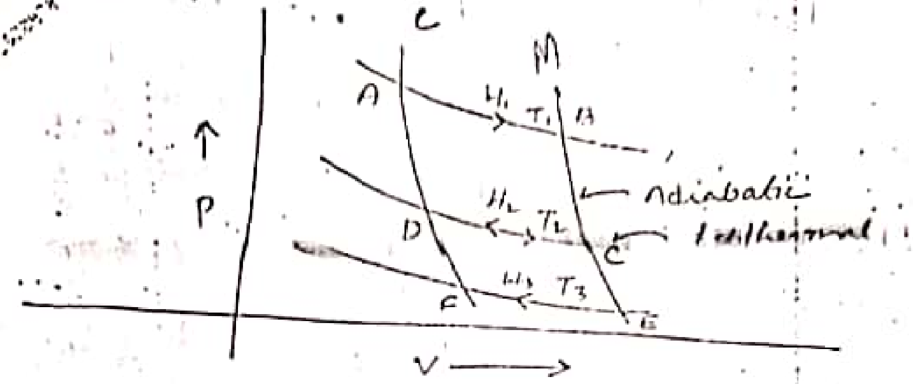
change in entropy, $dS = \frac{\delta H}{T}$ —①

In general the change in entropy $= \int_{S_1}^{S_2} dS = S_2 - S_1 = \int_A^B \frac{\delta H}{T}$ —②

But along the adiabatic, $\delta H = 0$, Therefore, the change in entropy along an adiabatic is zero or entropy remains constant.

Entrophy is a disorder of Thermodynamics system s the measurement of degree of disorder of state;

∴ $dS = \frac{dQ}{T}$ where, dQ = heat rejected by the system



Consider adiabatic L and M on the P-V diagram. ll along the adiabatic L with change in pressure here is in volume and temperature. This shows that all along the adiabatics L or M. There is change of temp ABCD represents the carnot's reversible cycle. From A to B heat energy H_1 s absorbed at temp. T_1 from C to D heat nergy H_2 is rejected at temp. T_2.

∴ $\frac{H_1}{T_1} = \frac{H_2}{T_2}$. similarly considering the cycle.

CEF.

$$\frac{H_2}{T_2} = \frac{H_3}{T_3}$$

Efficiency: The efficiency of the heat engine is the rate of quantity of heat converted into work, per cycle to the total amount of heat absorbed per cycle.

$$\therefore \text{Efficiency } \eta = \frac{\text{Useful Output}}{\text{Input}} = \frac{W}{H_1}$$

$$= \frac{H_1 - H_2}{H_1} = 1 - \frac{H_2}{H_1}$$

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

loss

[illegible] **Find the efficiency of a carnot's engine working between the steam point and the ice point.**

Here. ice point. $T_2 = 0°C = 273\ K$

steam point. $T_1 = 100°C = 373\ K$

$$\therefore \eta = 1 - \frac{273}{373} = 0.2681$$

$$\%\eta = 26.81\%$$

Q.5

KINETIC THEORY OF GASES:

Postulates of Kinetic theory of gases are given below:

① The gas is composed of small indivisible particles called molecules.

② The properties of the individual molecules are the same as that of the gas as a whole.

③ The distance between molecules is large as compared to that of a solid or liquid and hence the force of inter molecular attraction are negligible.

④ The molecules are continuously in motion with varying velocities and the molecules move in straight lines between two consecutive collisions.

⑤ The size of the molecules infinitesimally small as compared to the average distance traversed by molecule between two consecutive collision.

⑥ The molecules are perfectly hard elastic sphere and the whole of their energy in Kinetic.

80

Q. Expression for pressure exerted by a gas.

Brij lal - Heat and Thermodynamics. page -7.

Q. First law of thermodynamics states that the amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done.

$$dQ = dU + dW.$$

Q. Thermometry:

It is the measurement of thermometer.

THERMODYNAMICS

~~The~~ Zeroth law of thermodynamics:

In every measurement of temperature, the correctness of a law is tacitly assumed. This law, known as the zeroth law of thermodynamics, states that when any two bodies are each ~~sepor~~ separately in thermal equilibrium with a third, then they are also in thermal equilibrium with each other.

Constant volume hydrogen thermometre: (Gas thermometer) (Principle)

If 'γ' represents the co-efficient of increase of pressure at constant volume, then $P_{100} = P_0(1+\gamma \cdot 100)$. $P_0 = P_0(1+\gamma 0)$

or, $P_{100} - P_0 = P_0 \cdot 100\gamma$ ..... ①

Similarly, $P_t = P_0(1+\gamma t)$

$\therefore P_t - P_0 = P_0 \gamma t$ ..... ⑪

[illegible]ded ⑪ by ① we get, $\frac{t}{100} = \frac{P_t - P_0}{P_{100} - P_0}$

$$\therefore t = \frac{P_t - P_0}{P_{100} - P_0} \times 100.$$

⊛ It is based on the principle that when volume of gas is kept constant, the pressure increases with the rising temperature.

[illegible]tre: $R \propto t$. (Principle)

)

on the material of the wire used.

^{3} and $\beta = -5.8 \times 10^{-7}$.

$(1+\alpha t)$ ..... ①

$(1+\alpha \cdot 100)$ ..... ⑪

we get, $R_t - R_0 = R_0 \alpha t$.

$R_{100} - R_0 = R_0 \alpha \times 100$.

$$= \frac{R_t - R_0}{R_{100} - R_0} \times 100$$

⊛ It is based on the priciple of change of resistance with respect to temperature

① T. [illegible] form[illegible]

② The [illegible]

③ The meas

④ The cali br.

one of

form of

of the system

[illegible] wire.

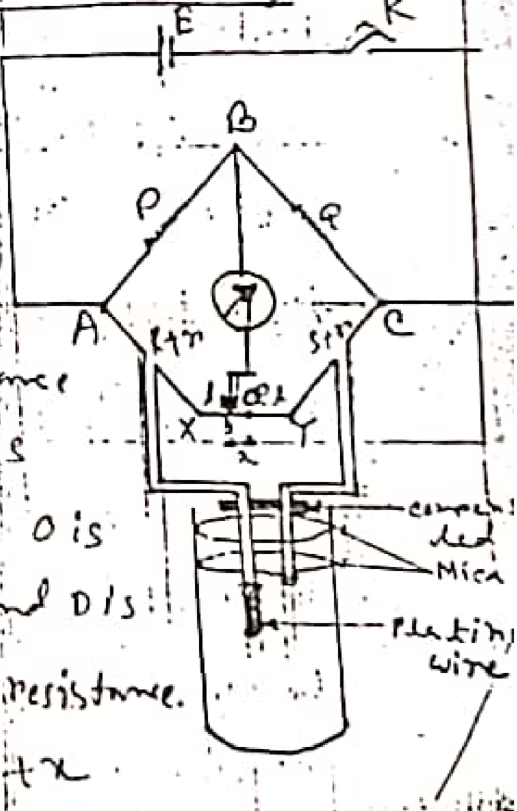
⑨ advantages and disadvantages of N_2 gas thermometer:

constant volume thermometer gas can be used over a wide range of ~~thermometer~~ temperature with H_2 gas and platinum-irridium bulb. The range is -200°c to 500°c

By using N_2 gas we can measure temperature upto 1500°C.

By using He gas we can measure temp. below -200°C

08.05 Construction of platinum resistance thermometer (Calender and Griffith's bridge)



There is a inductive less coil. P and Q are the standard resistance, R is the resistance of the platinum wire. r is the resistance of the compensating leds. XY is the bridge wire of length 2l. O is the center of the bridge wire and D is the null point. S is a standard resistance.

∴ XD = l-x and DY = l+x

plidation of the first law thermodynamics.

Thermomedric property of thermometer:

① dizign or construction ; ⓘⓘ colification

ⓘⓘⓘ sensetiveness

Thermomedric property of following thermometer

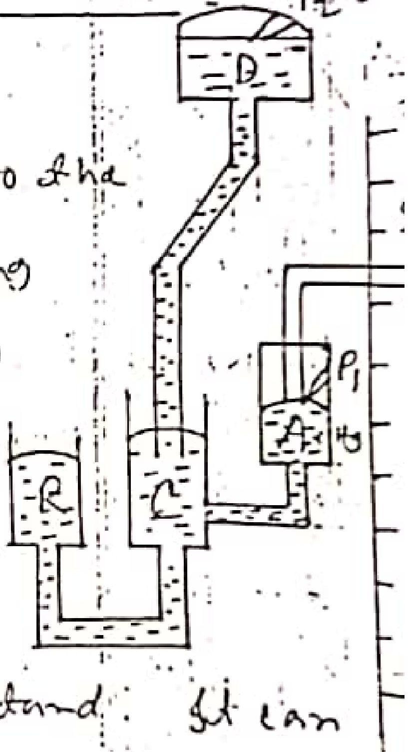
① Liquid thermometer: expansion or comprision of volume w.r. to temperature (Marcury, Hg)

② Gas thermometer: constand volume, expansion or compresion of pressure w. r. to temperature (Hydrogen gas ; H_2)

③ Resistance thermometer: change of resistance w.r. to temper (Platinum ; Pt)

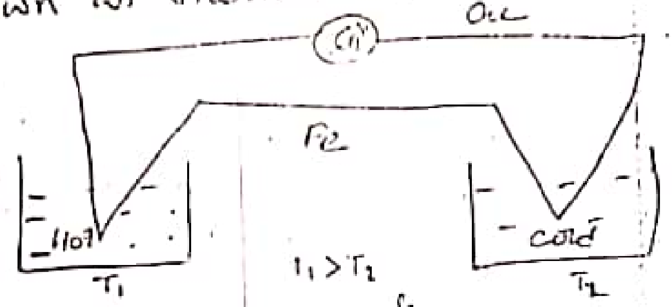
C.T. Construction of H_2 gas thermometers

It consists of a platinum-irridium bulb B connected to the tube A. Resourver R containing murcary (Hg) is connected to the tubes C and A as shown in the figure. A moveable barometric tube with a ... b. D is planned to a stand. It can ... moved vertically as desired. P_1 and P_2 ... ships vertical line.



rocouple Thermometer:

Principle: If two wires of dissimilar metal be joined at two ends and if the two junctions be maintained at two different temperatures one higher than the other, the emf is set up, which causes a current to flow in the circuit as indicated by the deflection produced in a galvanometer G included in the circuit. Two metals arranged in this way form a thermocouple and the current produced by the difference in temp. is known as thermo current.



Thermo emf;

Points to be noted for a thermocouple thermometer

① The choice of two different suitable elements forming them thermocouple.

② The electrical insulation of the wire.

③ The measurement of the EMF developed in the circ

④ The calibration of the thermocouple.

∴ from equ^{n} ③,

$$\frac{1}{2}(mN)c^2 = \frac{3}{2}RT$$

$$\Rightarrow \frac{1}{2}mc^2 = \frac{3}{2}\left(\frac{R}{N}\right)T$$

$$\Rightarrow \frac{1}{2}mc^2 = \frac{3}{2}KT \quad [K \rightarrow \text{bolsman constant}]$$

$$\Rightarrow E = \frac{3}{2}KT \text{ —— ④}$$

From equ^{n} ④, the main kinetic energy of a molecule directly propotional to the absolute temperature of a gas.

Thus at absolute zero (0) temp. the kinetic energy should be zero (0). It means at absolute zero (0) temp. the molecules are in a perfect state of rest and have no kinetic energy.

'04

C.T. (A) Degrees of freedom:

The total number of independent variables required to describe completely the state of motion of a body are called its degrees of freedom.

RMS velocity as a function of absolute temperature : (Energy $\propto$ T)

The pressure of a gas according to kinetic theory,

$$P = \frac{1}{3} \rho c^2$$

$$\Rightarrow P = \frac{1}{3} \frac{M}{V} c^2$$

$$\Rightarrow PV = \frac{1}{3} M c^2 \quad \text{—} ①$$

Considering one gm molecule of the gas at temp T K,

$$PV = RT \quad \text{—} ②$$

From eqn ① and ②,

$$\frac{1}{3} M c^2 = RT$$

$$\Rightarrow \frac{1}{2} M c^2 = \frac{3}{2} RT \quad \text{—} ③$$

Let the mass of each molecule be m and Avogadro's no. be N,

$$\therefore M = m \times N$$

$$\therefore XD = l - x \text{ and } DY = l + x$$

x is the distance betn the centre O and the null point D.

Let us consider, resistance of per unit length of bridge wire is ρ. So, total resistance is $2l\rho$,

we know, $\frac{P}{Q} = \frac{R}{S}$ —①

If $P = Q$, then from eqn ①:

$$1 = \frac{R}{S}$$

$$\therefore R = S$$

we can write, $R + r_1(l-x)\rho = S + r + (l+x)\rho$

$$\therefore R = S + 2x\rho \quad \text{—②}$$

'08, '05

Q advantages and disadvantages of resistance thermometer:

This can be used to measure temp. range from $-200°C$ to $1200°C$

'08, '05

Q Correction:

$$R_t = R_0(1+\alpha t+\beta t^2)$$

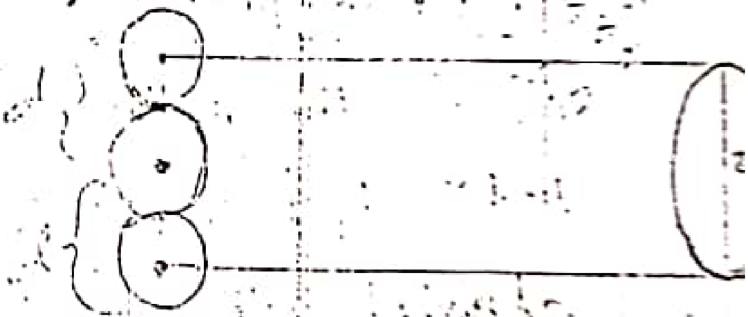
this is the standard eqn, not neglecting β though β is too small.

the free path is not constant. Therefore the term mean free path is used to indicate the mean distance travelled by a molecule betn two collisions. If the total distance travelled after N collision is S, then mean free path,

$$\lambda = \frac{S}{N} \quad —①$$

07 Ⓑ Mean free path, $\lambda \propto \frac{1}{d^2}$

Let us consider a molecule of diameter d and velocity v unit



∴ Area, $A = \pi d^2$

∴ Volume of cylinder, $V = \pi d^2 v$.

If per cc no. of molecules is n, the total no. of molecule $= \pi d^2 v . n$

∴ $XD = d - x$ and $DY = d + x$

Thus, the energy associated with each degree of freedom is $\frac{1}{2}KT$. This represents the theorum or law of equiapartitioni of energy.

It states that for any dynamical system in thermal equilibrium, the total energy is divided equally among all the degrees of freedom and the energy associated per degree of freedom is $\frac{1}{2}KT$.

07

(8) C.T.

Mean free path:

The path covered by a molecule betn two consecutive collision in a straight line is called free path.

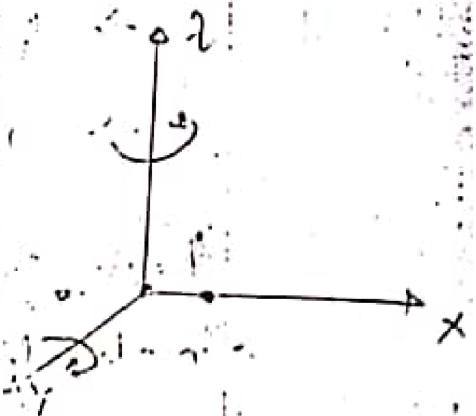
The direction of a molecule is changed after each collision. After a no. of collisions, the total path appears to be zig-zag and

Q.3, 10

Law of equiapartition of energy :

According to kinetic theory of gases, the mean kinetic energy of a gas molecule at a temp. T is given by,

$$\frac{1}{2}mc^2 = \frac{3}{2}KT$$



But, $c^2 = u^2 + v^2 + w^2$

As x, y and z are all equivalent, mean square velocities along these axes are equal

$\therefore u^2 = v^2 = w^2$

Hence, $u^2 = v^2 = w^2 = \frac{1}{2}c^2$

$\Rightarrow \frac{1}{2}mu^2 = \frac{1}{2}mv^2 = \frac{1}{2}mw^2$

$\therefore \frac{1}{2}mc^2 = 3\left[\frac{1}{2}mu^2\right] = 3\left[\frac{1}{2}mv^2\right] = 3\left(\frac{1}{2}mw^2\right) = \frac{9}{2}kT$

$\therefore \frac{1}{2}mu^2 = \frac{1}{2}KT$

$\frac{1}{2}mv^2 = \frac{1}{2}KT$

$\frac{1}{2}mw^2 = \frac{1}{2}KT$

$\therefore XD = d - x$ and $DY = d + x$

∴ Total no. of collisions, $N = \pi d^2 v n$

∴ Free path, $\lambda = \frac{v}{N}$

$$= \frac{v}{\pi d^2 v n}$$

$$= \frac{1}{\pi d^2 n}$$

$$= \frac{m}{\pi d^2 m n}$$

$$= \frac{m}{\pi d^2 \rho} \quad (\because \rho = mn)$$

As m, π and ρ are constant,

$$\lambda \propto \frac{1}{d^2}$$

According to Boltzman, $\lambda = \frac{3}{4\pi d^2 n}$

" to maxwell, $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$

Derivation of gas eqn

From Kinetic theory,

$$P = \frac{1}{3}\rho c^2$$

$$= \frac{1}{3}\frac{m}{V}c^2$$

$$\therefore PV = \frac{1}{3}mc^2$$

considering one gram of molecule of a gas at an absolute temp. T. The mean energy of the molecules,

$$= \frac{1}{2}mc^2$$

$$= \frac{1}{2}mNc^2$$

$$\therefore PV = \frac{1}{2}mNc^2$$

$$= \frac{2}{3}N \cdot \frac{1}{2}mc^2 \quad \text{—} ①$$

mean kinetic energy of a molecule $= \frac{1}{2}mc^2$

$$= \frac{3}{2}KT$$

From eqn ①, $PV = \frac{2}{3}N \cdot \frac{3}{2}KT$

$$\therefore PV = NKT$$

$\therefore XD = d-x$ and $DY = d+x$

force per unit area on the wall BCF
of ADEH is equal to the pressure P_x

$$\therefore P_x = \frac{m}{l \times l^2}\left(u_1^2+u_2^2+u_3^2+\cdots+u_n^2\right)$$

Similarly the pressure,

$$P_y = \frac{m}{l^3}\left(v_1^2+v_2^2+\cdots+v_n^2\right)$$

and $P_z = \frac{m}{l^3}\left(w_1^2+w_2^2+\cdots+w_n^2\right)$.

As the pressure is same in all directions

$$P = \frac{P_x+P_y+P_z}{3}$$

$$= \frac{m}{3l^3}\left[\left(u_1^2+v_1^2+\cdots+w_1^2\right)+\left(u_2^2+v_2^2+w_2^2\right)+\cdots + \left(u_n^2+v_n^2+w_n^2\right)\right]$$

$$= \frac{m}{3l^3}\left[c_1^2+c_2^2+c_3^2+\cdots+c_n^2\right] \quad \textcircled{1}$$

Let c be the root-mean-square velocity of the molecules, then $c^2 = \frac{c_1^2+c_2^2+\cdots+c_n^2}{n}$

$$\therefore nc^2 = c_1^2+c_2^2+\cdots+c_n^2$$

$\therefore XD = l-x$ and $DY = l+x$

considering a molecule P moving in a random direction with a velocity c_1. The velocity can be resolved into three mutually perpendicular components u_1, v_1 and w_1 along the x, y and z axes respectively.

$$c_1^2 = u_1^2 + v_1^2 + w_1^2$$

The component of the velocity with which the molecule P will strike the opposite face BCFG is u_1 and the momentum of the molecule is mu_1.

This molecule is reflected back with the same momentum mu_1 in an opposite direction and after travelling a distance l will strike the opposite face ADFH

$\therefore XD = l - x$ and $DY = l + x$

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∴ from eqnⁿ ①,

$$P = \frac{m}{3V} n c^2 \qquad [\because l^3 = V = \text{Volume}]$$
——②.

But, $M = mn$; where, M = mass of gas of V (volume),

m = mass of each molecule

n = no. of molecule in a volume V

$pv = \frac{2}{3} \cdot \frac{1}{2} mc^2$
$= \frac{2}{3} \frac{E}{V}$

∴ from eqnⁿ ②,

$$P = \frac{Mc^2}{3V} = \frac{M}{V} \cdot \frac{c^2}{3}$$

$$\therefore P = \frac{1}{3} \rho c^2 \quad \text{——③} \quad [\because \frac{M}{V_1} = \rho = \text{density}]$$

$$\Rightarrow c^2 = \frac{3P}{\rho}$$

$$\therefore c = \sqrt{\frac{3P}{\rho}}$$

④ Kinetic interpretation of Temperature:

considering a system of N molecules of monoatomic gas. If E is the total energ of the system, then some of the energy wi

..g......

be in the form of translational energy and the remaining may be rotational, vibrational potential energies of the molecules.

Let E_t be the translational energy then according to the law of equipartition of energy,

$$\frac{E_t}{N} = \frac{3}{2} KT \quad \text{①}$$

[K → Boltzmann constant

But $\frac{E_t}{N}$ is nothing but the average translational energy per molecule,

$$\bar{\varepsilon}_1 = \frac{E_t}{N} = \frac{3}{2} KT$$

08, 05, 02

$$\therefore \bar{\varepsilon}_1 \propto T$$

C.T. Ⓡ **Change in entropy in a reversible process :**

From A to B the process is isothermal,

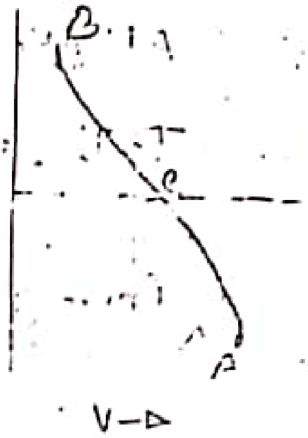
$\therefore$ Entropy, $S_1 = \frac{H_1}{T_1}$

$\therefore XD = d-x$ and $DY = d+x$

1,03

Estimation of critical constants:

considering the critical isothermal ACB as shown in figure. At the critical point C, the curve is horizontal. Therefore at point C, the curve $\left(\frac{dP}{dV}\right) = 0$.



At this point, the tangent also crosses the curve. Therefore the tangent at such a point is said to be stationary and the point is called 'the point of inflexion'. At the point of inflexion, $\frac{d^2P}{dV^2} = 0$.

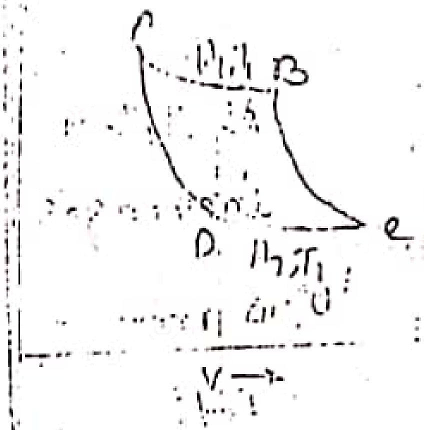
Hence at critical point C, $\frac{dP}{dV} = 0$ and $\frac{d^2P}{dV^2} = 0$

The van der waal's eqn is $\left(P + \frac{a}{V^2}\right)(V-b) = RT$.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{———} \; ①$$

$$\therefore \frac{dP}{dV} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \quad \text{——} \; ②$$

from B to C the process is adiabatic. So the change in entropy is zero (0).



from C to D the process is isothermal. so, the change in entropy, $S_2 = \frac{H_2}{T_1}$

from D to A the process is adiabatic. So, the change of entropy is zero (0)

So, the gain of entropy of the working substance during the cycle ABCDA $= \frac{H_1}{T_1} - \frac{H_2}{T_2}$

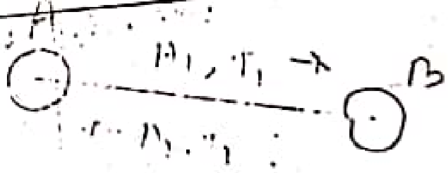
We know for a reversible process the loss of energy is zero (0). That is why,

$$\frac{H_1}{T_1} - \frac{H_2}{T_2} = 0$$

$$\therefore dS = 0 \quad [\text{constant}]$$

08

Change in entropy in a irriversible process:



loss in entropy $= \frac{H_1}{T_1}$

gain in " $= \frac{H_2}{T_2}$

∴ Change in entropy = $\frac{H_2}{T_2} - \frac{H_1}{T_1}$

As $T_1 > T_2$, thus the entropy of the system increases in irreversible process.

Q10 Prove that for a Diatomic gas $\gamma = 1.40$

Proof: Energy associated with each degree of freedom $= \frac{1}{2}KT$

∴ Energy associated with 5 degree of freedom $= \frac{5}{2}KT$

Considering 1 gm molecule of gas.

energy associated with 1 gm molecule of a diatomic gas $= N \times \frac{5}{2}KT = \frac{5}{2}NKT$

$$\therefore U = \frac{5}{2}KT$$

and $C_v = \frac{dU}{dT}$

But, $C_p - C_v = R$

$$\therefore C_p = C_v + R = \frac{5}{2}R + R = \frac{7}{2}R$$

Therefore the ratio of specific heats.

∴ $XD = d - x$ and $DY = d + x$

The change in momentum due to the impact is, $mu_1 - (-mu_1) = 2mu_1$

∴ The time ~~impact~~ interval bet^n two successive impacts on the wall BCFG is $\frac{2l}{u_1}$ seconds.

∴ No. of impacts per second $= \frac{1}{\frac{2l}{u_1}} = \frac{u_1}{2l}$

Change in momentum produced in one second due to this molecule $= 2mu_1 \times \frac{u_1}{2l}$

$$= \frac{mu_1^2}{l}$$

The force F_x due to the impact of all the molecules in one second

$$= \frac{m}{l}\left[u_1^2 + u_2^2 + u_3^2 + \cdots\cdots + u_n^2\right]$$

and $\frac{d^2P}{dV^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$ ——③

At the critical point C,

$T=T_c$, $P=P_c$, $V=V_c$, $\frac{dP}{dV}=0$ and $\frac{d^2P}{dV^2}=0$

from ①, $P_c = \frac{RT_c}{(V_c-b)} - \frac{a}{V_c^2}$ ——④

from ②, $0 = -\frac{RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3}$

$\Rightarrow \frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3}$ ——⑤

from ③, $0 = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4}$

$\Rightarrow \frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4}$ ——⑥

dividing ⑤ by ⑥,

$\frac{V_c-b}{2} = \frac{V_c}{3}$

$\Rightarrow 3V_c - 3b = 2V_c$

$\therefore V_c = 3b$ ——⑦

∴ [illegible] and [illegible] = 1+x

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from ⑤,

$$\frac{RT_c}{(3b-b)^2} = \frac{2a}{(3b)^3}$$

$$\Rightarrow \frac{RT_c}{4b^2} = \frac{2a}{27b^3}$$

$$\therefore T_c = \frac{8a}{27bR} \quad \text{———} ⑧$$

From ④, $P_c = \frac{8aR}{27bR(3b-b)} - \frac{a}{(3b)^2}$

$$= \frac{8a}{27\times 2b^2} - \frac{a}{9b^2}$$

$$= \frac{a}{9b^2}\left(\frac{8}{6}-1\right) = \frac{a}{9b^2}\times\frac{1}{3}$$

$$\therefore P_c = \frac{a}{27b^2} \quad \text{———} ⑨$$

'05

Physical importance of entropy:

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

or, $S_B - S_A = \int_A^B \frac{dQ}{T}$

① Just like temp. remains constant in isothermal process, the entropy remains constant in an adiabatic process

But $N \times k = R$

$\therefore PV = RT$

where, P = pressure = dynes/cm^2

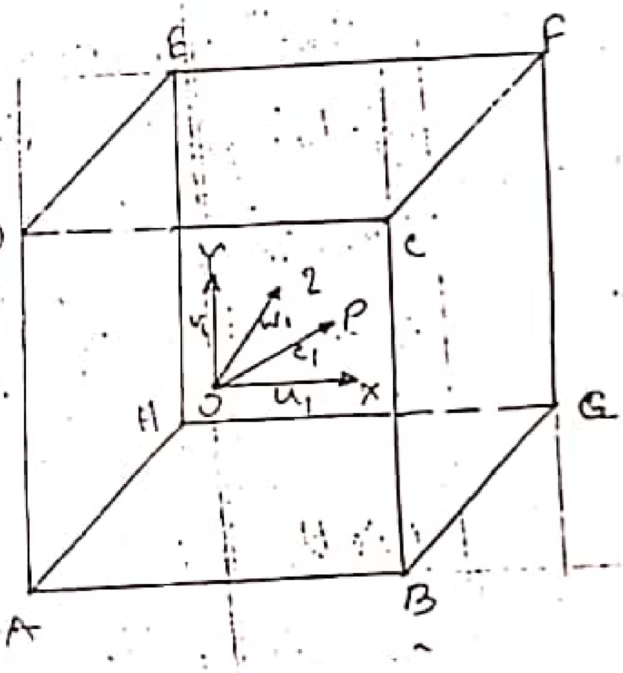
$R = 8.31 \times 10^7$ ergs/gm mol-K

T = absolute temp. = Kelvin (K)

V = volume of per gm molecule

'06, '03

Expression for the pressure exerted by a gas:



Considering the cubical vessel ABCDEFGH of side l cm containing gas.

$\therefore$ volume of the vessel $= l^3$ cm^3

Let, m = mass of each molecule

n = no. of molecules present in vessel

② It is a definite single valued function of the thermodynamic variables describing the state of a working substance.

③ In every natural process (i.e. irreversible change) there is always an increase in entropy

④ The 2nd law of thermodynamics can be stated in terms of entropy of a system.

⑤ Due to increase in entropy, unavailable energy increases.

⑥ According to Freeman Dyson, the entropy is a measure of disorderness. This disorderness can be evaluted by using the relation,

$$S = K \log W$$

where K is the Boltzman constant and W is the disorder parameter.

$\therefore XD = l - x$ and $DY = l + x$