

CHAPTER -2-

Equations of state

Intensive and extensive variables:

An intensive variable is one whose value is independent of the mass of a system. e.g. P, T, ρ density, η viscosity, v specific volume, v velocity, specific enthalpy, thermal, u conductivity. The volume on the other hand, is proportional to the mass of the system considered and is an example of an **extensive variable**, e.g. V volume, heat capacity, entropy, m , charge, magnetization, internal energy, kinetic energy, potential energy.

Any extensive variable, when divided by the mass or the number of moles of a system becomes **an intensive variable**, the ratio of an extensive variable to the mass of a system is called the specific value of that variable,

v = specific volume or the volume per unit mass,

V = total volume of a system.

M = mass of the system

$$v = \frac{V}{m} \quad \text{-----} \quad (1)$$

the specific volume is the reciprocal of the density ρ

$$\rho = \frac{m}{V} = \frac{1}{\frac{V}{m}} = \frac{1}{v} \quad \text{-----} \quad (2)$$

density (ρ) is an intensive variable and hence the specific volume is also .

The ratio of the extensive variable to the number of moles of a system is called the molal specific value of that variable .

$$v = \frac{V}{n} \quad \text{-----} \quad (3) \quad \text{molal specific volume}$$

$$n = \frac{m}{M} \quad \text{where } M = \text{molecular weight,} \quad n = \frac{N}{N_o}$$

$$v = \frac{V}{\frac{m}{M}} = M \frac{V}{m} = Mv = M \frac{1}{\rho} \quad \text{-----} \quad (4)$$

N is number of molecules, N_0 Avogadro's number = 6.025×10^{23} molecules / mole.

Note: that in the mks system, the term " mole" implies kilogram –mole , that is , a mass in kilograms numerically equal to the molecular weight . thus one mole O_2 means 32 kilograms of O_2 .

Equation of state

The equation of state of a substance is a relation between its P , V and T . we known by experience that an equation of state exists for every homogeneous substance solid , liquid , or gas .

$$f (p , v , T) = 0 \quad \text{-----} \quad (5)$$

Equation of state of an ideal gas

Suppose one has measured the p , v , t and mass of a certain gas, over wide ranges of these variable . Instead of the actual volume V, we shall use the molal specific volume , $v = \frac{V}{n}$. let us take all data collected at a given absolute

T, calculate for each individual measurement the ratio $\frac{pV}{T}$, and plot these ratios as ordinates against the P as abscissas . we shall use the mks system of units , in which P is expressed in $\frac{N}{m^2}$ and molal specific volume in $\frac{m^3}{kgm.-mole}$.

it is found experimentally that these ratios all lie on a smooth curve , whatever the T, but that the ratios at different temperatures. lie on different curves . The data for CO_2 are plotted in Fig-1 for a number of different temperatures.

The remarkable feature of these curves is a// that they all converge to exactly the same point on the vertical axis, whatever the temperature, and b// that the curves for all other gases converge to exactly the same point. This limit of the ratio $\frac{pV}{T}$, common to all gases , is called the universal gas constant and is denoted by R

$$R = 8.3149 \times 10^3 \text{ Joules/Kgm.-mole-deg. In mks system -----} \quad (6)$$

It follows that at low P we can write , for all gases ,

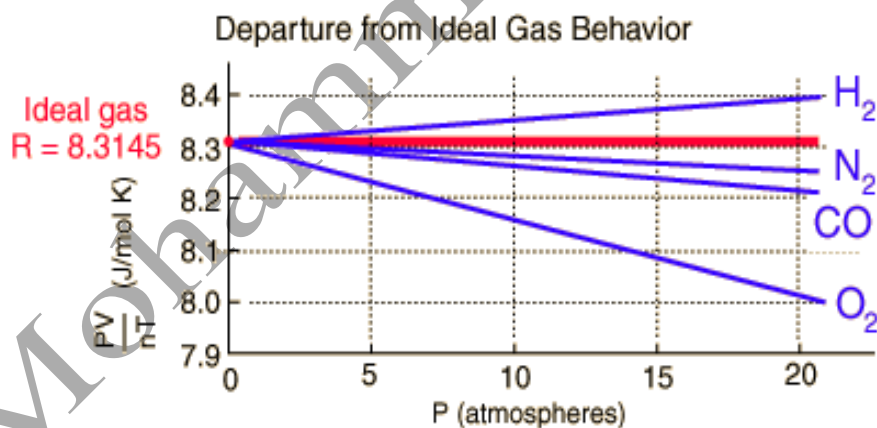
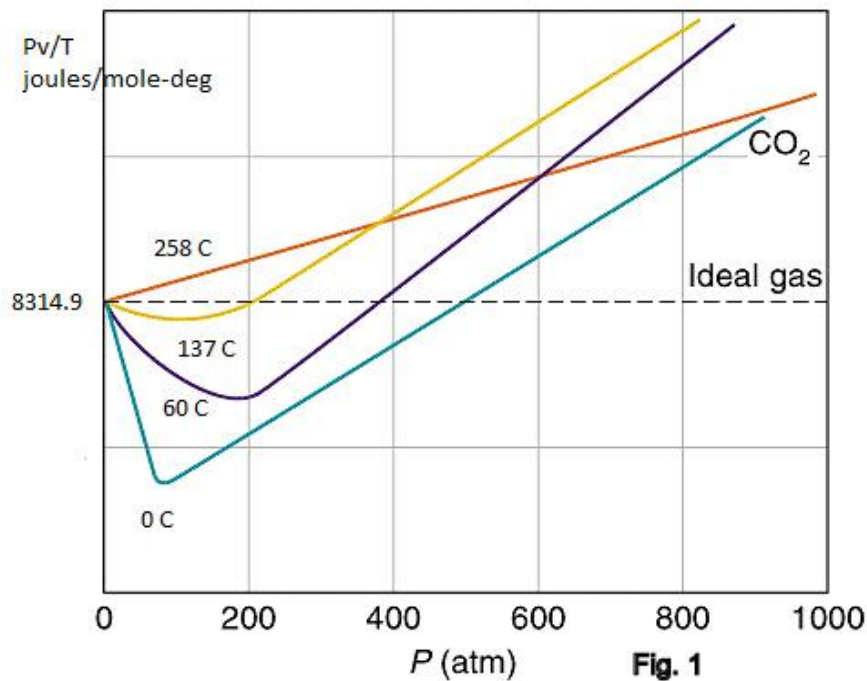
$$\frac{pV}{T} = R , \quad pV = RT , \quad \text{or} \quad pV = nRT \quad \text{-----} \quad (7)$$

$$R = 0.08206 \frac{\text{liter - atm.}}{\text{gm. - mole - deg}} \quad \text{Where p in atm .}$$

$$R = 8.3149 \times 10^7 \frac{\text{ergs}}{\text{gm.} - \text{mole} - \text{deg}}$$

In cgs system

Where p in dynes / cm^2 , v in cm^3



At low p , $Pv = RT$ for ideal gas $Pv = RT$ at all pressures and temperatures.
 It follows from eq.(7) that at standard condition's
 ($p = 1$ atmosphere = $1.01325 \times 10^5 \text{ n/m}^2$, $T = 273.16^\circ \text{ K} = 0^\circ \text{ C}$)

$$v = \frac{RT}{p} = \frac{8.3149 \times 10^3 \times 273.16}{1.01325 \times 10^5} = 22.4146 \frac{\text{m}^3}{\text{kgm} - \text{mole}}$$

At constant temp. the product of pressure and specific volume of an ideal gas is constant . if we plot the P as a function of v, as in fig .(2) ,we obtain at ant given T a rectangular hyperbola , with different hyperbolas temps. Real gases, of course, approximate to this behavior at low pressures, a fact that was discovered in (1660) by Robert Boyle and known as Boyle's law.

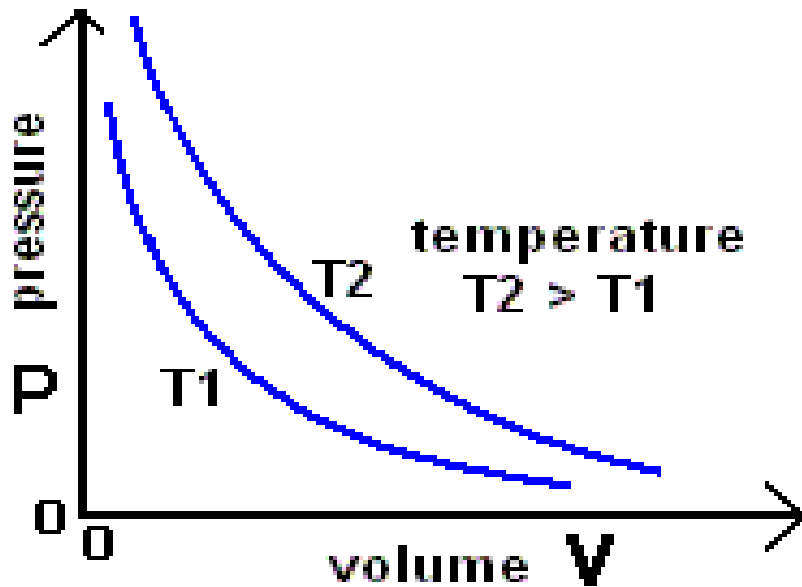


Fig. 2

Other equations of state :

Many equations have been proposed which describe the P-v-T relations of real gases more accurately than does the equation of state of an ideal gas. Some of these are frankly empirical while others are derived from assumptions regarding molecular properties. The Dutch Physicist van der Waals, in 1873, derived the following equation:

$$(P + \frac{a}{v^2})(v - b) = RT \quad \text{-----} \quad (8)$$

van der Waals Equation of state :

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

1// the size of molecule of the gas is negligible and.

2// the force of inter-molecular attraction are absent but in actual practice, at high pressure, the size of the molecules of the gas become significant and cannot be neglected in comparison with the volume of the gas. Also at high pressure, the molecules come closer and the force of intermolecular attraction are appreciable. Therefore, correction should be applied to the gas equation.

1// correction for pressure :

A molecule in the interior of a gas experiences forces of attraction in all directions and the resultant cohesive force is zero. A molecule near the walls of the container experiences a resultant force in words (away from the wall). Fig! (3). Due to this reason the observed pressure of the gas is less than the actual pressure. The correction for pressure P depends upon:

- a// The number of molecules striking unit area of the walls of the container per second and,
 - b// The number of molecules present in a given volume .
- Both these factors depend on the density of the gas.

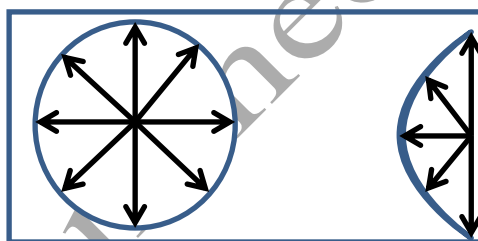


Fig. 3

Correction for pressure $p' \propto \rho^2 \propto \frac{1}{V^2}$ $P' \propto \rho^2 \propto \frac{1}{V^2}$

$$P' = \frac{a}{V^2} \quad \text{-----} \quad (9)$$

a is a constant

Hence correct pressure = $P + P' = P + \frac{a}{V^2}$ ----- (10)

2// correction for volume :

The fact that the molecules have finite size shows that the actual space for the movement of the molecules is less than the volume of the vessel. The molecules have the sphere of influence around them and due to this factor,

the correction for volume is b where b is approximately four times the actual volume of the molecules .

Therefore the corrected volume of the gas = $v - b$ ----- (11)

Let the radius of one molecule be r

The volume of the molecule = $X = \frac{4}{3}\pi r^3$ ----- (12)

The center of any two molecules can approach each other only by a minimum distance of $2r$ i.e. the diameter of each molecule. The volume of the sphere of influence of each molecule, S

$$S = \frac{4}{3}\pi(2r)^3 = 8X \quad \text{-----} \quad (13)$$

Consider a container of volume V . if the molecules are allowed to enter by one,

The volume available for first molecule = V

// // // second // = $V - S$

// // // third // = $V - 2S$

// --- // --- // --- nth // --- = $V - (n-1) S$

Average space available for each molecule

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

$$= V - \frac{S}{n} [1 + 2 + 3 + \dots + (n-1)] = V - \frac{S}{n} X \frac{(n-1)n}{2}$$

$$= V - \frac{nS}{2} + \frac{S}{2}$$

As the number of molecules is very large $S/2$ can be neglected .

$$\text{Average space available for each molecule} = V - \frac{nS}{2}$$

$$= V - \frac{8nX}{2} \quad \text{but } S = 8X \quad \text{from equation (13)}$$

$$= V - 4(nX) = V - b \quad \text{-----} \quad (14)$$

$b = 4(nX) =$ four times the actual volume of the molecule

Thus the van der Waals equation of state for a gas is

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad \text{-----} \quad (15)$$

Where \underline{a} and \underline{b} are van der Waals constants from eq. (15)

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \quad \text{-----} \quad (16)$$

Graphs between pressure and volume at various temperatures.

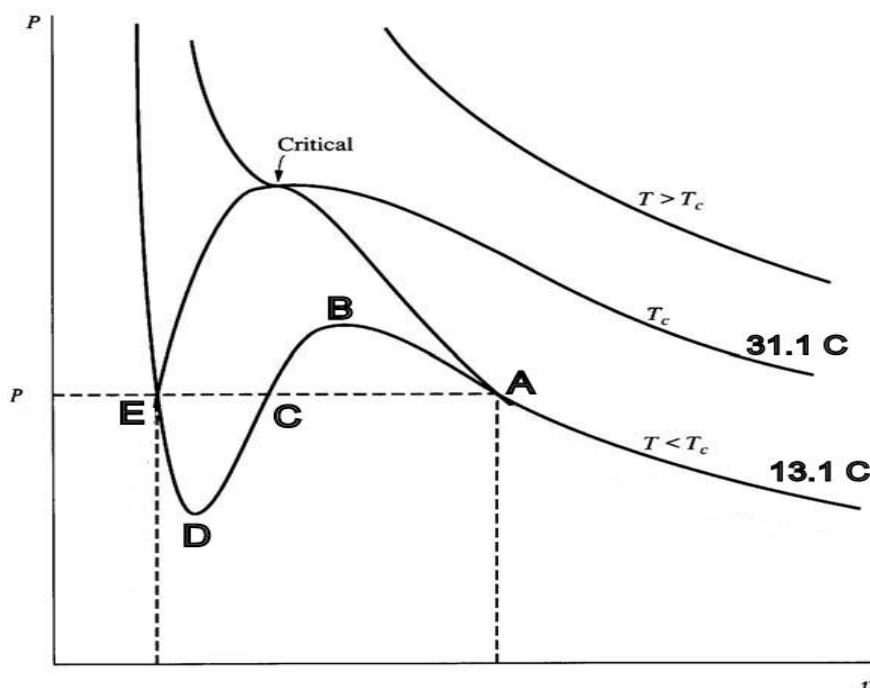


Fig. 4

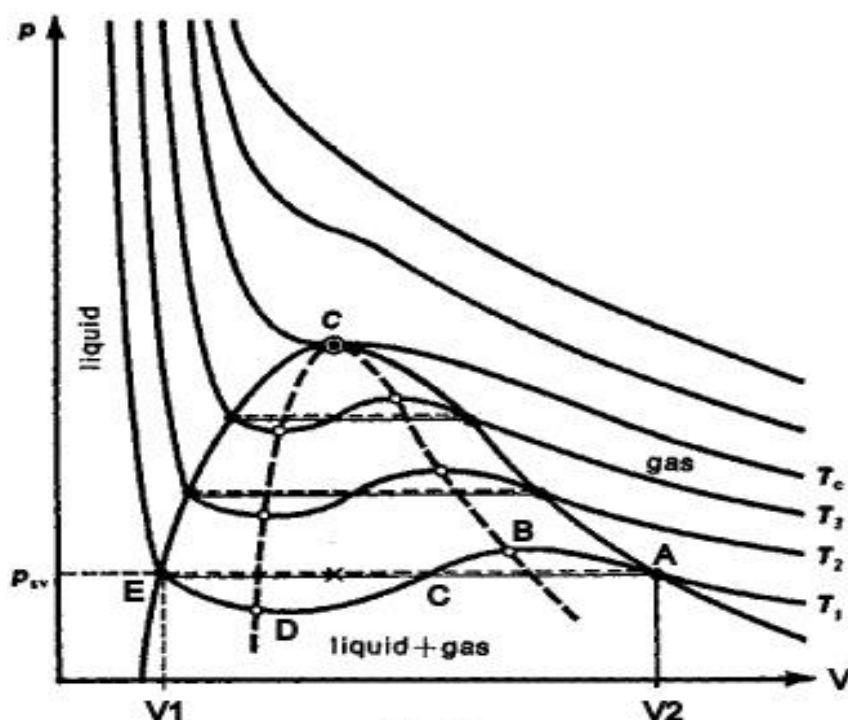


fig 4

are drawn using equation (15). The graphs are as shown in fig.(4). In the graph, the horizontal portion is absent. But in its place, the curve ABCDE is obtained. This does not agree with the experimental isothermals for CO₂ as obtained by Andrews. However, the portion AB has been explained as due to super cooling of the vapors (ينتج من فوق تبريد البخار), and the portion ED due to super heating of the liquid (فوق تسخين السائل). But the portion BCD cannot be explained because it shows decrease in volume with decrease in pressure, it is not possible in actual practice. The states AB and ED, though unstable, can be realized in practice by careful experimentation. At higher temperatures, the theoretical and experimental isothermals are similar. Until now as many as 56 different equations of state have been suggested. But no single equation satisfies all the observed facts. Dieterice (1901) has suggested an eq.

$$P(v-b) = RTe^{-\frac{a}{RTv}}$$

Berthelot has suggested an eq.

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

Critical constants

The critical temperature and the corresponding values of pressure and volume at the critical point are called the critical constants, At critical point, the rate of change of pressure with volume ($\frac{dp}{dv}$) is zero. This point is called the point of inflexion according to van der Waals eq.

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{----- (16) differentiating P with respect to v}$$

$$\frac{dp}{dv} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} \quad \text{----- (17)}$$

At the critical point $\frac{dp}{dv} = 0$, $T = T_c$, $v = v_c$

$$\frac{2a}{v_c^3} = \frac{RT_c}{(v_c - b)^2} \quad \text{----- (18)}$$

Differentiating eq. 17 $\frac{d^2p}{dv^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}$

At the critical point $\frac{d^2p}{dv^2} = 0$, $T = T_c$, $v = v_c$

$$\frac{6a}{v_c^4} = \frac{2RT_c}{(v_c - b)^3} \quad \text{----- (19) dividing eq. 18 by eq. 19}$$

$$\frac{2a}{v_c^3} = \frac{RT_c}{(v_c - b)^2}, \quad \frac{v_c}{3} = \frac{v_c - b}{2}, \quad 2v_c = 3v_c - 3b, \quad \underline{v_c = 3b} \quad \text{----- (20)}$$

Substituting the value of $v_c = 3b$ in eq. 18

$$\frac{2a}{(3b)^3} = \frac{RT_c}{(3b - b)^2}, \quad \frac{2a}{27b^3} = \frac{RT_c}{4b^2}, \quad \underline{T_c = \frac{8a}{27Rb}} \quad \text{----- (21)}$$

Substituting these values of v_c and T_c in eq. 16 $P = \frac{RT}{v-b} - \frac{a}{v^2}$

$$P_c = \frac{R \frac{8a}{27Rb}}{3b - b} - \frac{a}{(3b)^2}, \quad P_c = \frac{8aR}{27b \times 2b} - \frac{a}{9b^2}$$

$$\underline{P_c = \frac{a}{27b^2}}, \quad \text{----- (22)}$$

Questions

Q.(1) Calculate the value of critical temperature for carbon dioxide given that $a = 8.74 \times 10^{-3}$ atms., and $b = 2.3 \times 10^{-3}$ Cm³. Assuming $P = 1$ atm., $v = 1$ Cm³, and $T = 0^\circ\text{C} = 273$ K, the corresponding value of R can be obtained by substituting the values of P , v , a , b and T in the van der Waals equation.

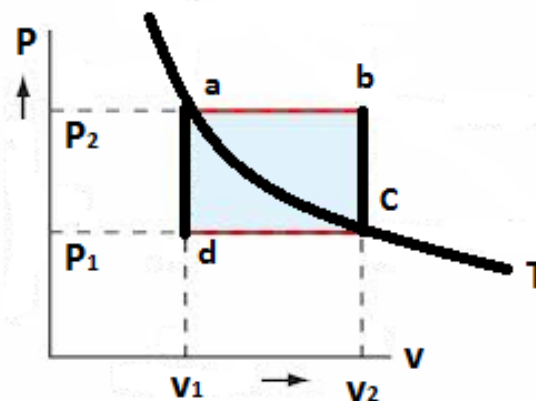
Q.(2) Calculate the van der Waals constants for dry air, given that $T_C = 132$ K, $P_C = 37.2$ atms., R per mole = 82.07 Cm³ atoms.K⁻¹.

Q.(3) The density of water in cgs units is $\frac{1\text{gm.}}{\text{Cm}^3}$. Compute: (a) the density in mks units, (b) the specific volume in $\frac{\text{m}^3}{\text{Kgm.}}$, (c) the mks molal specific volume.

(d) make the computation for air at standard conditions were the density in cgs units is 1.29×10^{-3} gm/Cm³. The mean molecular weight of air of air is 29 kgm., that is, the mass of 1kgm.-mole of air is 29kgm..

Q.(4) At standard condition, how many kilograms of air are there in a room measuring 10mX10mX3m?. The mean molecular weight of air is 29, that is, the mass of 1 kgm – mole of air is 29 kgm. What is the weight of the air , in pounds?

Q.(5) In Fig let $P_2 = 10 \times 10^5$ n/m², $P_1 = 4 \times 10^5$ n/m², $v_1 = 2.5$ m³/kgm.-mole. Find: (a) the temperature T , (b) the temperature at points b and d, (c) the specific volume v_2 , (d) the actual volume \underline{V} at point a if the system consists of 4kgm – mole of hydrogen, (e) the mass of gas if it is oxygen and if $V_1 = 5$ m³.

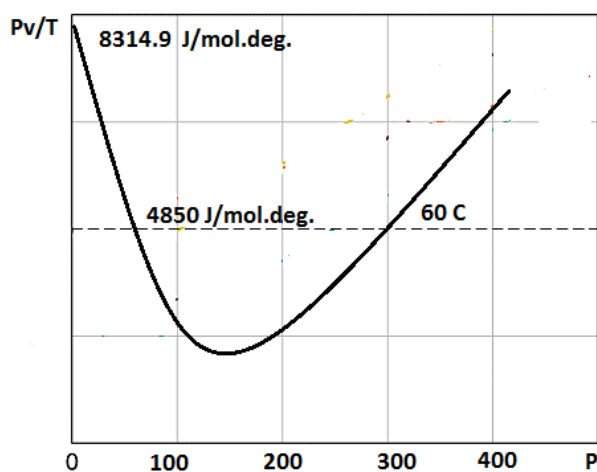


Q.(6) A tank of volume 0.5 m^3 contains oxygen at an absolute pressure of 150 atm. and a temperature of 20°C . Assume that oxygen behaves like an ideal gas. (a) How many kilogram – moles of oxygen are there in the tank?. (b) How many kilograms? (c) How many pounds? (d) Find the pressure if the temperature is increased to 500°C . (e) At a temperature of 20°C , how many moles can be withdrawn from the tank before the pressure falls to 15 atm.?

Q.(7) A cylinder provided with a movable piston contains an ideal gas a pressure \underline{P}_1 , specific volume \underline{v}_1 , and temperature \underline{T}_1 . The pressure and volume are simultaneously increased so that at every instant \underline{P} and \underline{v} are related by the equation $P = K\underline{v}$, where \underline{k} is constant. (a) Express the constant \underline{K} in terms of the pressure \underline{P}_1 , the temperature \underline{T}_1 , and the gas constant R. (b) Construct the graph representing the process a above in the $p - v$ plane. (c) Find the temperature when the specific volume has doubled, if $T_1 = 200 \text{ K}$.

Q.(8) One standard atmosphere is defined as the pressure produced by a column of mercury exactly 76 Cm. high, at a temperature of 0°C , and at a point where $g = 980.665 \text{ Cm/sec}^2$. (a) why do the temperature and the acceleration of gravity have to be specified in this definition?. (b) Compute the pressure in n/m^2 produced by a column of mercury 76 Cm in height, of density 13.6 gm/Cm^3 , at a point where $g = 980 \text{ Cm/sec}^2$.

Q.(9) (a) Estimate as accurately as you can from Fig. the molal specific volume of CO_2 at a pressure of 300 atm. and a temperature of 60°C . (b) At this pressure and temperature, how many moles of CO_2 are contained in a tank of volume 0.5 m^3 ?. (c) How many moles would the tank contain if CO_2 were an ideal gas?.



Q.(10) In all so – called diatomic gases, some of the molecules are dissociated into separate atoms, the fraction dissociated increasing with increasing temperature. The gas as a whole thus consists of a diatomic and a monatomic portion. Even though each component may act as an ideal gas, the mixture does not, because the number of moles varies with the temperature. The degree of dissociation δ of a diatomic gas is defined as the ratio of the mass m_1 of the monatomic portion to the total mass m of the system. $\delta = \frac{m_1}{m}$.

Show that the equation of states of the gas is

$$PV = (\delta + 1) \left(\frac{m}{M_2} \right) RT$$

Where M_2 is the molecular weight of the diatomic component. Assume that the gas obeys Daltons law, i.e., the measured pressure P is the sum of the pressures each component would exert if it alone occupied the total volume V .

Q.(11) Volume of the container is (0.0655cm^3), which contains O_2 , at pressure (2 atm.) and temperature (260°C). Find No. of, molecules and the mass of O_2 .