

विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।  
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचित: मानव धर्म प्रणेता  
सद्गुरु श्री रणछोड़दासजी महाराज

**STUDY PACKAGE** This is TYPE 1 Package  
please wait for Type 2

**Subject : CHEMISTRY**

**Topic : GASEOUS STATE**

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**CLASSES**

Index .....the support

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6. Answer Key
7. 34 Yrs. Que. from IIT-JEE
8. 10 Yrs. Que. from AIEEE

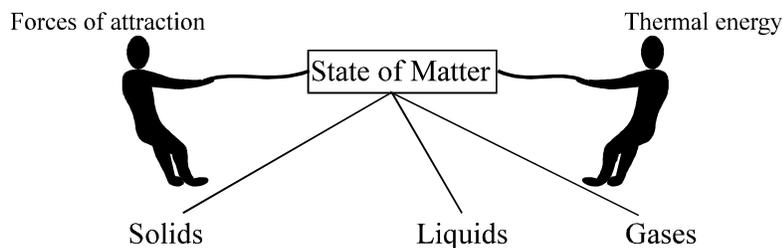
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## KEY CONCEPTS



### Parameters:

(i)	Forces of attraction			
(ii)	Thermal energy	down	moderate	up
(iii)	Space	down	moderate	up
(iv)	Shape	up	down	down
(v)	Volume	up	up	down
(vi)	Density	up	up	down

**GASEOUS STATE** : The state is characterized by sensitivity of volume change with change of pressure and temperature. It is due to large distance between molecules as compared to their own dimensions. There exists weak Vander Waal's forces, molecules move independent of each other with speed about  $400 \text{ m s}^{-1}$ .

??  
 (0,0) **Are volume of solids & liquid totally independent of pressure??**

**IDEAL GAS** : A gas with no intermolecular attractions & having very negligible volume occupied by molecules when compared with volume of gas is termed as ideal gas. A theoretical concept which for gases present can be obtained only under certain condition.

**REAL GAS** : Considerable forces of attraction & appreciable size of molecules. These under " certain conditions" behalve like ideal. [Refer : section of real gas behaviour]

**Parameter associated with the gas** :  $P, V, T, n$

where

**P** represents pressure exerted by the gas molecules on the walls of the container assuming negligible intermolecular attractions,

**V** represents free volume available for motion (equal to the volume of the container),

**T** represents absolute temperature, **n** represents no of moles.

**Conversion factors** : Pressure  $\rightarrow 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} = 760 \text{ mm of Hg} = 760 \text{ torr} = 1.013 \text{ bar}$

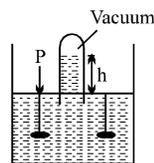
Volume  $\rightarrow 1 \text{ l} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3 = 1000 \text{ ml} = 1000 \text{ cm}^3$

Temperature  $\rightarrow T_K = T_C^\circ + 273 = \frac{5}{9} T_F^\circ + 255.22$

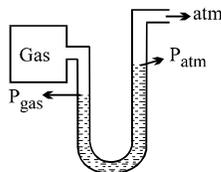
## INSTRUMENTS FOR PRESSURE CALCULATIONS :

**Barometer :**  $P = \frac{A \times h \times d \times g}{A}$

where  $d$  = density of fluid  
 $h$  = vertical height  
 $g$  = acceleration due to



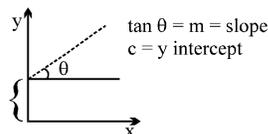
**Manometer :**  $P_{\text{gas}} = P_{\text{atm}} + hdg$



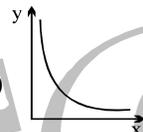
## EQUATION & GRAPHS OF EXTENSIVE UTILITY IN GASEOUS STATE :

*Two Parameters 'y' & 'x' if are related as*

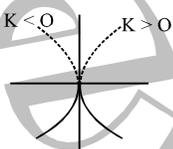
- (a)  $y = m x + C$  (where  $m$  &  $C$  are constants) [then there will be a direct relationship between them & graph will be a straight line as shown ]  
 $y = mx + C$  (straight line)



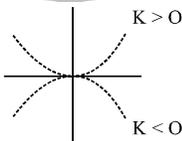
- (b)  $xy = \text{constant}$  (rect hyperbola) /  $y = \frac{m}{x} + C$  (where  $m$  &  $C$  are constant)



- (c)  $y^2 = Kx$  ( $K$  is a constant)



- (d)  $x^2 = Ky$  ( $K$  is a constant)



**Experimental Gas laws** → Relationship between various parameter of the gas. Gaseous state is the only state that allows a quantitative descriptive between the four parameters,  $P$ ,  $V$ ,  $T$  &  $n$ . The relationship which connects the four variables is known as equation of state, which can be obtained experimentally from the following gas laws.

# All are based on experimental data.

# All are applicable for ideal gases only.

# Get yourselves comfortable with all the various types of graphs to get a 'feel' of them.

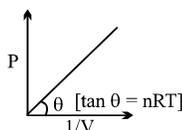
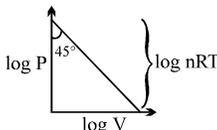
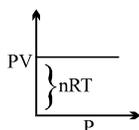
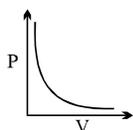
### I. Boyle's law

$$V \propto \frac{1}{P}$$

( $T$ , constant)  
 $n$  constant

$$P_1 V_1 = P_2 V_2$$

graphs are Isotherms





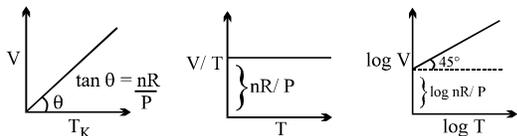
Plot the different curves for difference values of n & V to compare.

II. **Charle's law**

$$V \propto T \quad (P, \text{ constant})$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

graphs are **Isobars**



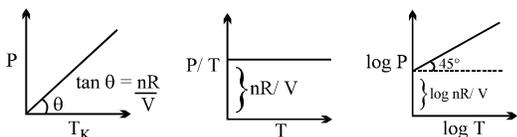
Plot graphs of V vs T<sub>c</sub> & V vs T<sub>F</sub>

III. **Gay Lussac's law**

$$P \propto T \quad (V, \text{ constant})$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

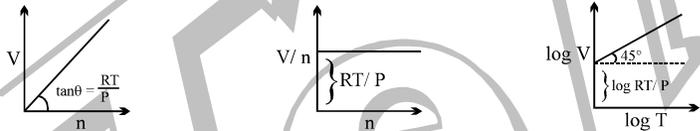
graphs are **Isochor**



IV. **Avogadro's law**

$$V \propto n \quad (T, P \text{ constant})$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$



**Combined Gas Law :**

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

**Equation Of State :**  $PV = nRT$

d = density of gas

$$\Rightarrow PV = \frac{W}{M} RT \quad R = \text{Universal Gas constant} = 0.0821 \text{ atm litres /kelvin/mol}$$

$$\Rightarrow PM = dRT \quad = 8.314 \text{ joule/kelvin} = 2\text{cal / kelvin/mol}$$

**Dalton's law of partial pressure :**

$$P_{\text{total}} = P_A + P_B + \dots \quad ; \quad P_{\text{wet gas}} = P_{\text{dry gas}} + P_{\text{H}_2\text{O vapour}} \quad \text{i.e. aq. tension.}$$

$$P_A, P_B \text{ are partial pressures.} \quad ; \quad P_A = \text{mole fraction}_A \times \text{Total pressure}$$

$$\text{and \% of gas in mixture} = \frac{\text{Partial pressure}}{\text{Total pressure}} \times 100.$$

**Amagat's Law :**

The total volume of a mixture of gases is equal to the sum of the partial volumes of the constituent gases, at same Temperature & Pressure.

### Graham's law of Diffusion & Effusion :

$$r \propto \frac{1}{\sqrt{d}} \quad \text{or} \quad r \propto \frac{1}{\sqrt{M}} \quad r \propto \frac{P}{\sqrt{M}} \quad [\text{For gases effusing at different pressures}]$$

$r$  is rate of diffusion of any gas.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad ; \quad \frac{\text{volume / time}}{\text{volume / time}} = \sqrt{\frac{M_2}{M_1}} \quad \mathbf{d}$$
 is density at some temperature.

$$r = \frac{\text{moles diffused}}{\text{time taken}} = \frac{\text{distance travelled in a narrow tube}}{\text{time taken}} = \frac{\text{Pressure drop I}}{\text{Pressure drop II}}$$

??  $\left(\frac{0.1}{0}\right)$  It should be noted that the rate of diffusion or effusion actually depends on pressure difference of the gas and not simply on its pressure. Moreover the pressure difference is to be measured for this gas only i.e. if a container holds [He] at a pressure of 0.1 atm and if a small pin-hole is made in the container and if the container is placed in a room, then the rate of effusion of He gas from the container to outside depends only on its pressure difference, which is 0.1-0 (as there is no He in the atmosphere). This implies that the diffusion of a gas is not dependent on the diffusion of any other gas.

??  $\left(\frac{0.1}{0}\right)$  Whenever we consider the diffusion of a gas under experimental conditions, we always assume that the gas diffuses in vacuum and during the time period for which the diffusion is studied the rate of diffusion (or the composition of diffusing or effusing mixture of gases) remains constant.

### Miscellaneous concepts used in Gaseous State:

(a) **Bursting of containers :** two concepts used depending upon type of container.

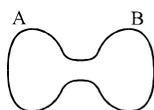
(i) **Bubble type** (very thin skin) cannot tolerate difference in pressure on the skin  
outside pressure = inside pressure

??  $\left(\frac{0.1}{0}\right)$  Any change in these cause change in volume & the container burst due to maximum stretching.

(ii) **Cylinder type** (thick skin) can withstand pressure difference till a limit but cannot have volume change.

??  $\left(\frac{0.1}{0}\right)$  Any change cause a change in pressure & when it exceeds the limits the container burst.

(b) **Connecting containers having gases**



??  $\left(\frac{0.1}{0}\right)$  On removal of nozzle the gas from higher pressure will travel so as to have equal pressure at both the containers.... from idea of total moles & final temperature each parameter can be calculated.

(c) **Changes in Open vessel :** Pressure of gas remains constant & so is the volume.

$$\therefore n_1 T_1 = n_2 T_2$$

(e) **Changes in closed vessel :**  $\frac{P_1}{n_1} = \frac{P_2}{n_2}$

- (f) **Barometric pressure distributor in a gas** [To calculate pressure at various height in a gas]

$$\ln \frac{P_2}{P_1} = \frac{-Mg}{RT} [H_2 - H_1] \quad P_2 = P_1 e^{-\frac{Mg}{RT} [H_2 - H_1]}$$

- (g) **I separation**

For separating lighter gas from a mixture.

**Separation Factor :**

$$f = \frac{n_1^1/n_2^1}{n_1/n_2} = f.$$

$n_1, n_2$  and  $n_1^1, n_2^1$  are the concentration of two isotopes before and after processing .

Theoretical separation factor  $f' = \sqrt{\frac{M_2}{M_1}}$

If required enrichment of species (1) is attained after 'x' times, then :

$$(f')^x = \frac{n_1^1/n_2^1}{n_1/n_2} = f.$$

Solving using Graham's law,  $x = \frac{2 \log f}{\log \left(\frac{M_2}{M_1}\right)}$

- (h) **Payload / lifting power** [based on Buoyancy]

L.P. of balloon =  $V (d - d_1)g - Mg$

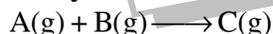
V = Volume of balloon

d = density of outside gas

$d_1$  = density of gas in the balloon

M = Mass of balloon

- (i) **Analysis of a reaction involving gaseous**



→ What happens to pressure as reaction proceeds (in a closed container)

- (j) **Vapour density and degree of dissociation**  $\alpha = \frac{D-d}{(n-1)d}$

**Kinetic theory of gases :**

$$P V = \frac{1}{3} m N u^2 = \frac{1}{3} M u^2 \text{ (For 1 mole)}$$

**Types of velocities :**

$$u^2 = \frac{u_1^2 + u_2^2 + \dots + u_N^2}{N} ; \quad u = \text{root mean square speed .}$$



Finds applications in K.E.

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}} ;$$

$$\text{Average speed} = \frac{u_1 + u_2 + \dots + u_N}{N} = \sqrt{\frac{8RT}{\pi M}}$$



Finds application in Collision theory

$$\text{most probable speed} = \sqrt{\frac{2RT}{M}}$$

$$\left. \begin{aligned} \text{most probable : average : r. m. s.} &= 1 : 1.13 : 1.22 \\ &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \end{aligned} \right\} \text{Relationship between three} \\ \text{types of speeds}$$

$$u_{\text{rms}} > u_{\text{av}} > u_{\text{mp}}$$

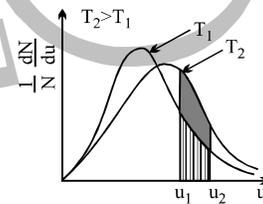
$$\text{Average kinetic energy of a single molecule} = \frac{3}{2} \cdot \frac{R}{N} \cdot T = \frac{3}{2} kT$$

$$k = \text{Boltzman constant} = 1.3806 \times 10^{-16} \text{ erg deg}^{-1}.$$

$$\text{Total kinetic energy for one mole of a gas} = \frac{3}{2} RT.$$

$$\text{kinetic energy of } n \text{ moles of a gas} = n \times \frac{3}{2} RT$$

$$\begin{aligned} \text{Maxwell distribution Laws: } dN_u &= 4\pi N \left( \frac{M}{2\pi RT} \right)^{3/2} \exp(-Mu^2/2RT) u^2 du \\ &= 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} \exp(-mu^2/2kT) u^2 du \end{aligned}$$



Collision frequency & Mean Free Path :

$$\text{Mean free path } \lambda = \frac{d_1 + d_2 + \dots + d_n}{n}$$

$$\lambda = \frac{\text{Average velocity / RMS velocity}}{\text{collision number or frequency}} = \frac{kT}{\sqrt{2} \pi \sigma^2 P}$$

$k$  = Boltzman constant ;  $\sigma$  = collision diameter .

$$Z_1 = \sqrt{2} \pi \sigma^2 \bar{u} N^* \text{ [collisions made by one molecule]}$$

$$Z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{u} N^{*2}$$

## THE REAL PATH

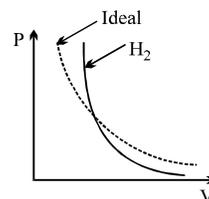
### Vander Waals equation of state :

$$\left( P + \frac{a}{V^2} \cdot n^2 \right) (V - nb) = nRT$$

a, b are Vander Waals constants ; different for each gas  
 unit of a  $\longrightarrow$  atm L<sup>2</sup> mol<sup>-2</sup> ; S.I. unit  $\longrightarrow$  Pa m<sup>6</sup> mol<sup>-2</sup>  
 unit of b  $\longrightarrow$  L mol<sup>-1</sup> ; S.I. unit  $\longrightarrow$  m<sup>3</sup> mol<sup>-1</sup>  
 greater the value of 'a' more easily the gas is liquefiable ;  
 greater the value of 'b' greater the molecular size ,

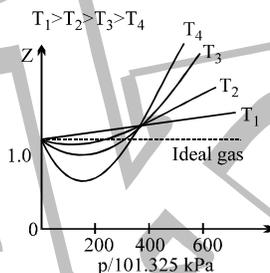
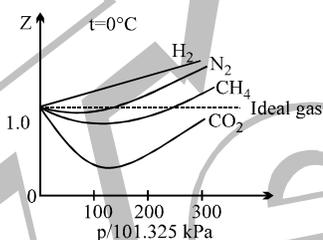
### Real gases : Deviation from ideal behaviour

The curve for the real gas has a tendency to coincide with that of an ideal gas at low pressures when the volume is large. At higher pressures, however deviations are observed.



### Compressibility factor :

$$z = \frac{PV}{nRT} = \frac{\text{volume observed}}{\text{volume ideal}}$$



### Boyle Temperature :

$$T_B = \frac{a}{bR}$$

### Inversion Temperature :

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

### Interpretation Of Deviation From Vander Waals Equation :

- (i) At low pressure  $z = \frac{PV}{RT} = 1 - \frac{a}{VRT}$
- (ii) At high pressure  $z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$
- (iii) At extremely low pressure  $z = \frac{PV}{RT} = 1$  ;  $Pb = \frac{a}{V}$

## HEAT CAPACITIES

$C_p$  = Molar heat capacity at constant pressure

$C_v$  = Molar heat capacity at constant volume

$c_p$  = specific heat capacity at constant pressure

$c_v$  = specific heat capacity at constant volume

$$\Rightarrow C_p - C_v = R$$

$$\Rightarrow \frac{C_p}{C_v} = r \quad r = 1.66 \text{ (monoatomic); } 1.4 \text{ (diatomic)}$$

### Molar Specific Heat :

= specific heat  $\times$  molecular mass

$$C_p - C_v = R/J ; \quad \frac{C_p}{C_v} = 1.66 \text{ for monoatomic ; } \frac{C_p}{C_v} = 1.4 \text{ for diatomic}$$

### Degree Of Freedom :

Three for monoatomic gas ; Five for diatomic gas .

For a molecule having N atoms, total are 3N

**Translational** : 3 for all types [at all temp.]

**Rotational** : 2 for linear  
3 for N-linear

**Vibrational** : 3N - 5 for linear  
3N - 6 for N-linear

Each contributing  $\frac{1}{2} KT$

Each contributing  $KT$

### Law Of Equipartition Of Energy :

**Translational Motion** :  $\bar{E}_{\text{trans}} = \frac{1}{2} mv^2 = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \Rightarrow \frac{3}{2} KT$

**Rotational Motion** :  $\bar{E}_{\text{rot}} = \frac{1}{2} I_x \omega_x^2, \frac{1}{2} I_y \omega_y^2$  (linear)

$$= \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 \text{ (N.L.)}$$

$$\therefore \text{linear} = KT ; \text{N.L.} = \frac{3}{2} KT$$

**Vibrational Motion** :  $\bar{E}_{\text{vib}} = \frac{1}{2} KT + \frac{1}{2} KT = KT$

### SOME OTHER EQUATION OF STATE

#### Dieterici Equation :

$$P e^{na/VRT} \times (V - nb) = nRT$$

#### Berthelot Equation :

$$\left( P + \frac{n^2 a}{T V^2} \right) (V - nb) = nRT \quad (\text{a \& b are Berthlot's constant different from vander Waal's constant})$$

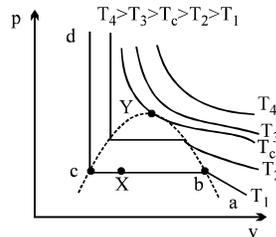
**Virial Equation Of State For 1 Mole Of Gas :**

$$z = \frac{P V}{R T} = 1 + B \frac{1}{V} + C \frac{1}{V^2} + D \frac{1}{V^3} + \dots \text{ (B, C, D... are temp. dependent constant)}$$

$$\left. \begin{aligned} B &= \text{second virial co-efficient} = b - \frac{a}{R T} \\ C &= \text{third virial co-efficient} = b^2. \end{aligned} \right\} \text{gas dependent}$$

**Critical Phenomenon : Critical Temp, Critical pressure, Critical volume**

$$T_c = \frac{8 a}{27 R b} ; P_c = \frac{a}{27 b^2} ; V_c = 3 b$$



**The law of corresponding states :**

$$p_r = \frac{p}{p_c}, \quad T_r = \frac{T}{T_c} \quad \text{and} \quad V_r = \frac{V_m}{V_c}$$

$$p = p_r p_c, \quad T = T_r T_c \quad \text{and} \quad V_m = V_r V_c$$

Substituting these expression in the van der Waals equation

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

we obtain  $\left( p_r p_c + \frac{a}{V_r^2 V_c^2} \right) (V_r V_c - b) = RT_r T_c$

Replacing  $p_c$ ,  $V_c$  and  $T_c$  in terms of  $a$ ,  $b$  and  $R$ , we get

$$\left\{ p_r \frac{a}{27 b^2} + \frac{a}{V_r^2 (3b)^2} \right\} \{ V_r (3b) - b \} = RT_r \left( \frac{8a}{27 R b} \right)$$

i.e.  $(p_r + 3/V_r^2) (3V_r - 1) = 8T_r$

$$Z = \frac{p V_m}{R T} = \frac{(p_r p_c)(V_r V_c)}{R(T_r T_c)} = \frac{p_c V_c}{T_c} \left( \frac{p_r V_r}{T_r} \right) = \frac{3 p_r V_r}{8 T_r}$$

## EXERCISE # I

### EXPERIMENTAL GAS LAW AND APPLICATION OF IDEAL GAS EQUATION.

- Q.1 3.6 gm of an ideal gas was injected into a bulb of internal volume of 8L at pressure P atmp and temp T-K. The bulb was then placed in a thermostat maintained at (T+ 15) K. 0.6 gm of the gas was let off to keep the original pressure. Find P and T if mol weight of gas is 44.
- Q.2 A toy balloon originally held 1.0 gm of He gas and had a radius 10 cm. During the night, 0.25 gm of the gas effused from the balloon. Assuming ideal gas behaviour, under these constant P and T conditions, what was the radius of the balloon the next morning.
- Q.3 If a scuba diver is to remain submerged for 1 hr, what pressure must be applied to force sufficient air into the tank to be used. Assume 0.5 dm<sup>3</sup> of air per breath at standard atmospheric pressure, a respiration rate of 38 breaths per minute, and a tank capacity of 30 dm<sup>3</sup>.
- Q.4 While resting, the average human male use 0.2 dm<sup>3</sup> of O<sub>2</sub> per hour at S T P for each kg of body mass. Assume that all this O<sub>2</sub> is used to produce energy by oxidising glucose in the body. What is the mass of glucose required per hour by a resting male having mass 60 kg. What volume, at S T P of CO<sub>2</sub> would be produced.
- Q.5 In a basal metabolism measurement timed at 6.00 min, a patient exhaled 52.5 L of air, measured over water at 20°C. The vapour pressure of water at 20°C is 17.5 torr. The barometric pressure was 750 torr. The exhaled air analyzed 16.75 vol% oxygen and the inhaled air 20.32 vol% oxygen, both on dry basis. Neglecting any solubility of the gases in water and any difference in the total volumes of inhaled and exhaled air, calculate the rate of oxygen consumption by the patient in ml (S.T.P) per minute.
- Q.6 One mole of NH<sub>4</sub>Cl is kept in an open container & then covered with a lid. The container is now heated to 600 K where all NH<sub>4</sub>Cl dissociates into NH<sub>3</sub> & HCl. If volume of the container is 24.63 litres, calculate what will be the final pressure of gases inside the container. Also find whether the lid would stay or bounce off if it can with stand a pressure difference of 5.5 atm. Assume that outside air is at 300 K and 1 atm pressure.

### DALTON'S LAW OF PARTIAL PRESSURE

- Q.7 12 g N<sub>2</sub>, 4 gm H<sub>2</sub> and 9 gm O<sub>2</sub> are put into a one litre container at 27°C. What is the total pressure.
- Q.8 1.0×10<sup>-2</sup> kg of hydrogen and 6.4×10<sup>-2</sup> kg of oxygen are contained in a 10×10<sup>-3</sup> m<sup>3</sup> flask at 473 K. Calculate the total pressure of the mixture. If a spark ignities the mixture. What will be the final pressure.

### GRAHAM'S LAW OF DIFFUSION AND EFFUSION

- Q.9 At room temp, NH<sub>3</sub> gas at one atmp & HCl gas at "P" atmp are allowed to effuse through identical pin holes to the opposite ends of a glass tube 1m long & uniform cross-section. A white deposit is observed at a distance of 60 cm from the HCl end. What is "P".
- Q.10 A gas mixture contains equal number of molecules of N<sub>2</sub> and SF<sub>6</sub>, some of it is passed through a gaseous effusion apparatus. Calculate how many molecules of N<sub>2</sub> are present in the product gas for every 100 molecules of SF<sub>6</sub>.

- Q.11 Two gases NO and O<sub>2</sub> were introduced at the two ends of a one metre long tube simultaneously (tube of uniform cross-section). At what distance from NO gas end, Brown fumes will be seen.
- Q.12 At 20 °C two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N<sub>2</sub> & other with 1 kg H<sub>2</sub>. The N<sub>2</sub> balloon leaks to a pressure of  $\frac{1}{2}$  atm in one hour. How long will it take for H<sub>2</sub> balloon to leak to a pressure of  $\frac{1}{2}$  atm.
- Q.13 Naturally occurring Fluorine is entirely <sup>19</sup>F, but suppose that it were 50% F<sup>19</sup> and 50% F<sup>20</sup> whether gaseous diffusion of UF<sub>6</sub> would then work to separate U<sup>235</sup> from U<sup>238</sup>.
- Q.14 Pure O<sub>2</sub> diffuses through an aperture in 224 sec, whereas mixture of O<sub>2</sub> and another gas containing 80 % O<sub>2</sub> diffuses from the same in 234 sec. What is molecular weight of the gas?
- Q.15 A space capsule is filled with neon gas at 1.00 atm and 290 K. The gas effuses through a pin-hole into outer space at such a rate that the pressure drops by 0.3 torr/sec
- (a) If the capsule were filled with ammonia at the same temperature and pressure, what would be the rate of pressure drop.
- (b) If the capsule were filled with 30.0 mol % helium, 20.0 mol % oxygen & 50.0 mol % nitrogen at a total pressure of 1.00 atm & a temp. of 290 K, what would be the corresponding rate of pressure drop.
- Q.16 The composition of the equilibrium mixture (Cl<sub>2</sub> ⇌ 2Cl) which is attained at 1200 °C is determined by measuring the rate of effusion through a pin hole. It is observed that at 1.8 mm Hg pressure, the mixture effuses 1.16 times as fast as Kr effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. [Kr = 84 a. m. u.]

**APPLICATION OF CONCEPT OF GASOUS STATE**

- Q.17 Show that the height at which the atmospheric pressure is reduced to half its value is given by
- $$h = \frac{0.6909 RT}{Mg}$$
- Q.18(a) How much H<sub>2</sub> (in mol) is needed to inflate a balloon of radius 3m to a pressure of 1 atm in an ambient temp at 25° C at sea level.
- (b) What mass can the balloon lift at sea level, where the density of air is 1.22 Kg m<sup>-3</sup>.
- (c) What would be the payload if He were used instead of H<sub>2</sub>.
- Q.19 Calculate the pressure of a barometer on an aeroplane which is at an altitude of 10 Km. Assume the pressure to be 101.325 Kpa at sea level & the mean temperature 243 K. Use the average molar mass of air (80% N<sub>2</sub>, 20 % O<sub>2</sub>)
- Q.20 Automobile air bags are inflated with N<sub>2</sub> gas which is formed by the decomposition of solid sodium azide (NaN<sub>3</sub>). The other product is Na - metal. Calculate the volume of N<sub>2</sub> gas at 27°C and 756 Torr formed by the decomposing of 125 gm of sod azide.
- Q.21 What will be the temperature difference needed in a hot air balloon to lift 1.0 kg of mass? Assume that the volume of balloon is 100 m<sup>3</sup>, the temperature of ambient air is 25 °C, the pressure is 1 bar, and air is an ideal gas with an average molar mass of 29 g mol<sup>-1</sup> (hot and cold both).

- Q.22 An iron cylinder contains helium at a pressure of 250 k pa and 27°C. The cylinder can withstand a pressure of  $1 \times 10^6$  pa . The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. [melting point of cylinder = 1800 k ]
- Q.23 Determine the molar mass of a gas if its pressure is to fall to one-half of its value in a vertical distance of one meter at 298 K.

**KINETIC THEORY OF GASEOUS LAW MAXWELL DISTRIBUTION OF SPEEDS**

- Q.24 The time taken for a given volume of gas E to effuse through a hole is 75 sec. Under identical conditions the same volume of a mix of CO & N<sub>2</sub> (containing 40% of N<sub>2</sub> by volume ) effused in 70 seconds. Calculate
- the relative mol mass of E , and
  - the RMS velocity ( in ms<sup>-1</sup> units ) of E at 0°C.
- Q.25 At what temperature in °C, the U<sub>rms</sub> of SO<sub>2</sub> is equal to the average velocity of O<sub>2</sub> at 27°C.
- Q.26 Calculate U<sub>rms</sub> of molecules of H<sub>2</sub> at 1 atmp density of H<sub>2</sub> is 0.00009 g/cc.
- Q.27 A bulb of capacity 1 dm<sup>3</sup> contains  $1.03 \times 10^{23}$  H<sub>2</sub> molecules & pressure exerted by these molecules is 101.325 kPa. Calculate the average square molecular speed and the temperature.
- Q.28 The mean kinetic energy of a molecule at 0°C is  $5.621 \times 10^{-14}$  ergs. Calculate the number of molecules in gm molecule of gas.
- Q.29 The density of CO at 273 K and 1 atm is 1.2504 kg m<sup>-3</sup>. Calculate (a) root mean square speed (b) the average speed and (c) most probable speed.
- Q.30 Calculate the temperature values at which the molecules of the first two members of the homologous series, C<sub>n</sub>H<sub>2n+2</sub> will have the same rms speed as CO<sub>2</sub> gas at 770 K. The normal b.p. of n-butane is 273 K. Assuming ideal gas behaviour of n-butane upto this temperature, calculate the mean velocity and the most probable velocity of its molecules at this temperature.
- Q.31 Calculate the temperature at which the root mean square velocity, average velocity and most probable velocity of oxygen gas are all equal to 1500 ms<sup>-1</sup>.
- Q.32 Calculate the fraction of N<sub>2</sub> molecules at 101.325 kPa and 300 K whose speeds are in the range of  $u_{mp} - 0.005 u_{mp}$  to  $u_{mp} + 0.005 u_{mp}$ .
- Q.33 What is the ratio of the number of molecules having speeds in the range of  $2u_{mp}$  and  $2u_{mp} + du$  to the number of molecules having speeds in the range of  $u_{mp}$  and  $u_{mp} + du$ ?

**COLLISIONS AMONG GASEOUS MOLECULES**

- Q.34 At low pressure and high temperature, the vander Waals equation is reduced to
- |                       |                                    |
|-----------------------|------------------------------------|
| (A) $PV_m = RT$       | (B) $(P + a/V_m^2) (V_m - b) = RT$ |
| (C) $P(V_m - b) = RT$ | (D) $(P + a/V_m^2) (V_m) = RT$     |

- Q.35 Calculate the mean free path in  $\text{CO}_2$  at  $27^\circ\text{C}$  and a pressure of  $10^{-6}$  mm Hg. (molecular diameter = 460 pm)
- Q.36 Calculate the value of  $\sigma$ ,  $\lambda$ ,  $Z_1$  and  $Z_{11}$  for nitrogen molecules at  $25^\circ\text{C}$  and at pressure of  $10^{-3}$  mm Hg. Given that  $b$  for nitrogen is  $39.1 \text{ cm}^3 \text{ mol}^{-1}$ .
- Q.37 A mixture of hydrogen and helium is prepared such that the number of wall collisions per unit time by molecules of each gas is the same. Which gas has the higher concentration?
- Q.38 The mean free path of the molecule of a certain gas at 300 K is  $2.6 \times 10^{-5}$  m. The collision diameter of the molecule is 0.26 nm. Calculate  
(a) pressure of the gas, and (b) number of molecules per unit volume of the gas.

**REAL GAS AND VANDER WAALS EQUATION OF STATE**

- Q.39 The density of mercury is  $13.6 \text{ g/cm}^3$ . Estimate the  $b$  value.
- Q.40 Calculate the pressure exerted by 22 g of carbon dioxide in  $0.5 \text{ dm}^3$  at 298.15 K using:  
(a) the ideal gas law and (b) vander waals equation. Given:  
[ $a = 363.76 \text{ kPa dm}^6 \text{ mol}^{-2}$  and  $b = 42.67 \text{ cm}^3 \text{ mol}^{-1}$ ]

**COMPRESSIBILITY FACTOR**

- Q.41 The compressibility factor for  $\text{N}_2$  at  $-50^\circ\text{C}$  and 800 atmp pressure is 1.95 and at  $100^\circ\text{C}$  and 200 atmp, it is 1.10. A certain mass of nitrogen occupied one litre at  $-50^\circ\text{C}$  and 800 atmp. Calculate the volume occupied by the same quantity of  $\text{N}_2$  at  $100^\circ\text{C}$  and 200 atmp.
- Q.42 At 273.15 K and under a pressure of 10.1325 MPa, the compressibility factor of  $\text{O}_2$  is 0.927. Calculate the mass of  $\text{O}_2$  necessary to fill a gas cylinder of  $100 \text{ dm}^3$  capacity under the given conditions.

**BOYLE'S TEMPERATURE CRITICAL PHENOMENON AND INVERSION TEMPERATURE**

- Q.43 The vander waals constant for  $\text{O}_2$  are  $a = 1.36 \text{ atm L}^2 \text{ mol}^{-2}$  and  $b = 0.0318 \text{ L mol}^{-1}$ . Calculate the temperature at which  $\text{O}_2$  gas behaves, ideally for longer range of pressure.
- Q.44 The vander Waals constants for gases A, B and C are as follows
- | Gas | $a/\text{dm}^6 \text{ kPa mol}^{-2}$ | $b/\text{dm}^3 \text{ mol}^{-1}$ |
|-----|--------------------------------------|----------------------------------|
| A   | 405.3                                | 0.027                            |
| B   | 1215.9                               | 0.030                            |
| C   | 607.95                               | 0.032                            |

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around STP?

**HEAT CAPACITY**

- Q.45 One mole of a non linear triatomic gas is heated in a closed rigid container from  $500^\circ\text{C}$  to  $1500^\circ\text{C}$ . Calculate the amount of energy required if vibrational degree of freedom become effective only above  $1000^\circ\text{C}$ .



## EXERCISE # II

Q.1 A 50 litre vessel is equally divided into three parts with the help of two stationary semi permeable membrane (SPM). The vessel contains 60 g H<sub>2</sub> gas in the left chamber, 160 g O<sub>2</sub> in the middle & 140 g N<sub>2</sub> in the right one. The left SPM allows transfer of only H<sub>2</sub> gas while the right one allows the transfer of both H<sub>2</sub> & N<sub>2</sub>. Calculate the final ratio of pressure in the three chambers.

Q.2 Militants are hiding at the top of the kargil peak which is 7000 m above the plains. Major of a troop of soldiers wants to send few soldiers to the peak to kill the enemies by balloons, then find the minimum volume of each balloon (volume remain constant throughout the mission) if he attach 10 balloons to each soldier. Given

(i) Change in density in atmosphere is  $d = d_0 e^{-Mgh/RT}$   
(where  $d_0$  is density at plain and  $d$  is density at height 'h')

(ii)  $M = 29$  gm/mole (constant)

(iii)  $T = 27^\circ\text{C}$  (constant)

(iv)  $g = 10$  m/sec<sup>2</sup>

(v) Each balloon contains 10 moles of H<sub>2</sub>

(vi) weight of each soldier is 75 kg.

Q.3 There are two vessels of same volume consisting same no of moles of two different gases at same temperature. One of the gas is CH<sub>4</sub> & the other is unknown X. Assuming that all the molecules of X are under random motion whereas in CH<sub>4</sub> except one all are stationary. Calculate  $Z_1$  for X in terms of  $Z_1$  of

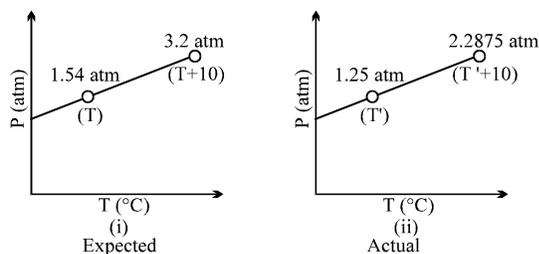
CH<sub>4</sub>. Given that the collision diameter for both the gases are same &  $(U_{\text{rms}})_x = \frac{1}{\sqrt{6}} (U_{\text{av}})_{\text{CH}_4}$ .

Q.4 A mixture of CH<sub>4</sub> & O<sub>2</sub> is used as an optimal fuel if O<sub>2</sub> is present in thrice the amount required theoretically for combustion of CH<sub>4</sub>. Calculate number of effusions steps required to convert a mixture containing 1 part of CH<sub>4</sub> in 193 parts mixture (parts by volume). If calorific value (heat evolved when 1 mole is burnt) of CH<sub>4</sub> is 100 cal/mole & if after each effusion 90% of CH<sub>4</sub> is collected, find out what initial mole of each gas in initial mixture required for producing 1000 cal of energy after processing.  
[Given  $(0.9)^5 = 0.6$ ]

Q.5 A closed vessel of known volume containing known amount of ideal gaseous substance 'A' was observed for variation of pressure with temperature. The expected graph was to be like as in (i) However actual observations revealed the graph to be like. (ii) The deviation was attributed to polymerisation of gas molecules as  $nA(g) \rightleftharpoons A_n(g)$ . If it is known that the above reaction gives only 50% yield

(a) Calculate the ratio of  $\frac{n_{\text{experiment}}}{n_{\text{theoretical}}}$  (where  $n_{\text{exp.}}$  = Total no. of gaseous mole acutally present  
 $n_{\text{theoretical}}$  = Total no. of mole original taken)

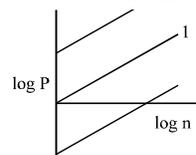
(b) Find the value of  $n$  to which the gas A is being polymerised into



Q.6 You are told to prepare a closed experimental environment (a box) for student mice. The box volume will be 294 liters (about 10 ft<sup>3</sup>) and the entire air volume will be changed every minute. The relative humidity of the air entering the box is to be controlled at 40% at 21°C. What weight of H<sub>2</sub>O must be added to the flow of dry air per minute? (Equilibrium vapour pressure for H<sub>2</sub>O at 21°C ≈ 19 torr). (R = 0.082 liter atm mole<sup>-1</sup>deg<sup>-1</sup> mol wt: H<sub>2</sub>O = 18)

Q.7 Graph between log P (atm) v/s log n is plotted for an ideal gas enclosed in 24.63 litre container at three different temperatures. If  $T_1 = \frac{T_2}{3} = 2T_3$  [where T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub> are temperature in kelvin of graph 1, 2 & 3] then

- Mention graph 2 & graph 3.
- Calculate T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>.
- Calculate slope of graphs 1, 2 & 3.
- Calculate intercept of graphs 2 & 3.



Q.8 During one of his adventure, Chacha chaudhary got trapped in an underground cave which was sealed two hundred year back. The air inside the cave was poisonous, having some amount of carbon monoxide in addition to O<sub>2</sub> and N<sub>2</sub>. Sabu, being huge could not enter into the cave, so in order to save chacha choudhary he started sucking the poisonous air out of the cave by mouth. Each time, he filled his lunge with cave air and exhaled it out in the surroundings. In the mean time fresh air from surrounding effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half of its initial value of one atmosphere.

If the initial sample of air from the cave contain 5% by volume CO.

If the safe level of CO in the atmosphere is less than 0.001% by volume how many times does Sabu need to such out air in order to save Chacha chaudhary.

Q.9 A compound exists in the gaseous state both as a monomer (A) and dimer (A<sub>2</sub>). The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in a vessel of volume 33.6 litres and heated to 273<sup>0</sup> C. Calculate the pressure developed, if the compound exists as a dimer to the extent of 50 per cent by weight, under these conditions. (R = 0.082)

Q.10 The following reaction is carried out in a flask at 101325 pascal and 383 k with the initial concentration of CH<sub>4</sub>, O<sub>2</sub> as 0.01 & 0.03 mole.



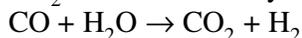
All reactants and products are gases at 383 k. A shortwhile after the completion of reaction the flask is cooled to 283 k at which H<sub>2</sub>O is completely condensed. Calculate :

- Volume of flask.
- Total pressure and partial pressure of various species at 383 k, 283 k.
- number of molecules of various substance before and after reaction.

Q.11 A closed vertical cylinder is divided into two parts by a frictionless piston, each part contains 1 mole of air . At 27 °C the volume of the upper part is 4 times than that of the lower part. Calculate the temperature when volume of the upper part will be three times than that of the lower part.

Q.12 A water gas mixture has the compisition by volume of 50% H<sub>2</sub>, 45% CO and 5% CO<sub>2</sub>.

(i) Calculate the volume in litres at STP of the mixture which on treatment with excess steam will contain 5 litres of H<sub>2</sub>. The stoichiometry for the water gas shift reaction is



- Find the density of the water gas mixture in kg/m<sup>3</sup>.
- Calculate the moles of the absorbants KOH, Ca(OH)<sub>2</sub> and ethanolamine.

HO-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub> required respectively to collect the CO<sub>2</sub> gas obtained.

Q.13 One mole of an ideal gas is subjected to a process in which  $P = \frac{1}{8.21} V$  where P is in atm & V in litre. If the process is operating from 1 atm to finally 10 atm (no higher pressure achieved during the process) then what would be the maximum temperature obtained & at what instant will it occur in the process.

Q.14 A gas present in a container connected to frictionless, weightless piston operating always at one atmosphere pressure such that it permits flow of gas outside (with no adding of gas). The graph of  $n$  vs T (Kelvin) was plotted & was found to be a straight line with co-ordinates of extreme points as (300, 2) & (200, 3). Calculate

- (i) relationship between  $n$  & T
- (ii) relationship between V & T
- (iii) Maxima or minima value of 'V'

Q.15 Find the critical constant ( $P_c$ ,  $V_c$  and  $T_c$ ) in terms of A and B, also find compressibility factor (z) for the following equation of state.

$$PV = RT - \frac{A}{V} + \frac{2B}{V^2}$$

where A and B are constant, P = pressure and V = molar volume.

Q.16 Calculate the volume occupied by 14.0 g  $N_2$  at 200 K and 8.21 atm pressure if  $\frac{P_c V_c}{RT_c} = \frac{3}{8}$  and

$$\frac{P_r V_r}{T_r} = 2.2.$$

### EXERCISE # III

**Question No. 1 to 3 are based on the following information. Read it carefully to answer the questions that follows.**

A gas undergoes dissociation as  $A_4(g) \longrightarrow 4A(g)$  in a closed rigid container having volume 22.4 litres at 273 K. If the initial moles of  $A_4$  taken before dissociation is 1 then

- Q.1 The total pressure (in atm) after 50% completion of the reaction (assuming ideal behaviour)  
(A) 1/2                      (B) 2.5                      (C) 2                      (D) 4
- Q.2 If the gases are not ideal & at the beginning total pressure observed is less than 1 atm then  
(A) compressibility factor of  $A_4 > 1$                       (B) compressibility factor of  $A_4 < 1$   
(C) compressibility factor of  $A_4 = 1$                       (D) compressibility factor of  $A > 1$
- Q.3 If the gases are non-ideal & after 100% dissociation total pressure is greater than 4 atm, then  
(A) The compression of A (g) will be easier than that of ideal gas  
(B) The compression of A (g) will be difficult than that of ideal gas  
(C) The compression of A (g) will be same as that of ideal gas  
(D) A cannot be compressed

**Question No. 4 to 6 are based on the following Passage. Read it carefully & answer the questions that follow**

Two containers X & Y are present with container X consisting of some mass of He at some temperature while container Y having double the volume as that of container X & kept at same temperature containing same mass of  $H_2$  gas as the mass of Helium gas. Based on this data & the following conditions answer the question that follows

**Assume sizes of  $H_2$  molecule & He atom to be same & size of H-atom to be half to that of He-atom & only bimolecular collisions to be occurring.**

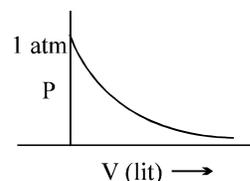
**Condition I:** all except one atom of He are stationary in cont. X & all molecules of  $H_2$  are moving in container Y.

**Condition II:** both containers contain all moving molecules

- Q.4 Assuming **condition I** to be applicable & if no. of *total collisions* occurring per unit time is 'A' in container X then no. of total collisions made by any one molecule in container Y will be:  
(A) A                      (B)  $\sqrt{2} A$                       (C)  $\frac{A}{\sqrt{2}}$                       (D) none of these
- Q.5 Assuming **condition II** then ratio of 'total no. of collisions per unit volume per unit time' in container X & container Y is (container X : container Y)  
(A) 1:1                      (B)  $\sqrt{2} : 1$                       (C)  $1 : \sqrt{2}$                       (D) 4:1
- Q.6 Assuming **condition II** to be applicable, if temperature only of container Y is doubled to that of original (causing dissociation of all  $H_2$  gas into H gaseous atoms) then, if no. of total collisions per unit volume per unit time in container X is A then, no. of total collisions made by all molecules per unit volume in container Y would be  
(A)  $2\sqrt{2} A$                       (B)  $\sqrt{2} A$                       (C)  $8\sqrt{2} A$                       (D) none of these

**Question No. 7 to 9 are based on the following Passage. Read it carefully & answer the questions that follow**

On the recently discovered 10<sup>th</sup> planet it has been found that the gases follow the relationship  $P e^{V/2} = nCT$  where C is constant other notation are as usual (V in lit., P in atm and T in Kelvin). A curve is plotted between P and V at 500 K & 2 moles of gas as shown in figure



- Q.7 The value of constant C is  
 (A) 0.01 (B) 0.001 (C) 0.005 (D) 0.002
- Q.8 Find the slope of the curve plotted between P Vs T for closed container of volume 2 lit. having same moles of gas  
 (A)  $\frac{e}{2000}$  (B)  $2000 e$  (C)  $500 e$  (D)  $\frac{2}{1000e}$
- Q.9 If a closed container of volume 200 lit. of O<sub>2</sub> gas (ideal gas) at 1 atm & 200 K is taken to planet. Find the pressure of oxygen gas at the planet at 821 K in same container  
 (A)  $\frac{10}{e^{100}}$  (B)  $\frac{20}{e^{50}}$  (C) 1 atm (D) 2 atm

**Question No. 10 to 11 (2 questions)**

For a gaseous molecular system the probability of finding a molecule with velocity between v and v + dv is given by

$$\frac{dN_v}{N} = \left(\frac{m}{kT}\right) e^{-mv^2/2kT} v dv$$

where m = mass of gas molecule  
 k = Boltzmann constant  
 T = Temperature of gas  
 N<sub>v</sub> = No. of molecules with velocity between v and v + dv  
 N = Total No. of molecules

- Q.10 At some temperature the fraction of molecules with kinetic energies between E and E + dE is given by  
 (A)  $\frac{1}{kT} e^{-E/kT} E dE$  (B)  $\left(\frac{m}{kT}\right) e^{-E/kT} dE$  (C)  $\frac{1}{kT} e^{-E/kT} dE$  (D)  $\left(\frac{m}{kT}\right) e^{-E/kT} E dE$
- Q.11 Fraction of molecules with K.E. greater than E is given by  
 (A)  $\int_0^E \frac{1}{kT} e^{-E/kT} dE$  (B)  $\int_E^\infty \frac{1}{kT} e^{-E/kT} E dE$  (C)  $\int_E^\infty \frac{1}{kT} e^{-E/kT} dE$  (D)  $\int_0^E \frac{1}{kT} e^{-E/kT} E dE$
- Q.12 Ratio of fraction of molecules with K.E. greater than and less than average K.E. is:  
 (A)  $\frac{1}{e^{1/2} + 1}$  (B)  $\frac{1}{e^{3/2} - 1}$  (C)  $\frac{e^{1/2}}{1 - e^{1/2}}$  (D)  $\frac{e^{3/2}}{e^{3/2} - 1}$

**Question No. 13 to 15 (3 questions)**

The rate of change of pressure (p) of a gas at constant temperature and constant external pressure due to effusion of gas from a vessel of constant volume is related to rate of change of number of molecules present by

$$\frac{dp}{dt} = \frac{kT}{V} \frac{dN}{dt}$$

where k = Boltzmann constant, T = temperature, V = volume of vessel & N = No. of molecules and

$$\frac{dN}{dt} = \frac{-pA_0}{(2\pi mkT)^{1/2}}, \text{ where } A_0 = \text{area of orifice and } m = \text{mass of molecule}$$

Q.13 Time required for pressure inside vessel to reduce to 1/e of its initial value is ( $\ln e = 1$ )

(A)  $\left(\frac{2\pi m}{kT}\right)^{1/2} \frac{V}{A_0}$     (B)  $\left(\frac{kT}{2\pi m}\right)^{1/2} \frac{V}{A_0}$     (C)  $\left(\frac{2\pi mkT}{A_0}\right)^{1/2}$     (D)  $\frac{2\pi m}{kT} \frac{V}{A_0}$

Q.14 If the gas inside the vessel had molecular weight 9 times the gas in previous example and area of orifice was doubled and temperature maintained at 4T, time required for pressure to fall to 1/e times of its initial value would be (t = answer of previous option)

(A) 1.33 t    (B) 4.24 t    (C) 0.75 t    (D) 1.125 t

Q.15 The incorrect statement(s) is/are

- [I] Pressure will not fall to zero in finite time
- [II] Time required for pressure to decrease to half its initial value is independent of initial pressure
- [III] The relations given above are true for real gases also

(A) I    (B) II    (C) III    (D) I and III

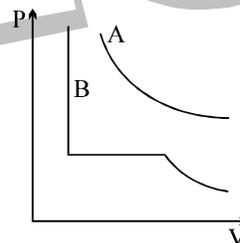
**Question No. 16 to 17 (2 questions)**

For two gases A and B, P v/s V isotherms are drawn at T K as shown.

$T_A$  &  $T_B$  are critical temperatures of A & B respectively

Q.16 Which of following is true?

(A)  $T_A < T < T_B$     (B)  $T_A > T > T_B$   
 (C)  $T_A > T_B > T$     (D) none of above



Q.17 The correct statement(s) is/are

- (I) Pressure correction term will be more negligible for gas B at T K.
  - (II) The curve for gas 'B' will be of same shape as for gas A if  $T > T_B$
  - (III) Gas 'A' will show same P v/s V curve as of gas 'B' if  $T > T_A$
- (A) III only    (B) II and III    (C) II only    (D) All

Q.18 n moles of Helium gas are placed in a vessel of volume V Liter. at T K. If  $V_I$  is ideal volume of Helium then diameter of He atom is

(A)  $\left[\frac{3}{2} \frac{V_I}{\pi N_A n}\right]^{1/3}$     (B)  $\left[\frac{3(V - V_I)}{2 \pi N_A n}\right]^{1/3}$     (C)  $\left[\frac{6(V - V_I)}{\pi N_A n}\right]^{1/3}$     (D)  $\left[\frac{6V_I}{\pi N_A n}\right]^{1/3}$

**Q.19 and Q.20 are based on the following passage.**

Under a given condition, it is found that two separate gases effuse out of two separate container in such

a way that they follows the equation  $\frac{dN}{dt} = -K_1N$  &  $\frac{dN}{dt} = -K_2N$ ,  $K_1=6.93 \times 10^{-3}\text{sec}^{-1}$ ,  $K_2=6.93 \times 10^{-5}\text{sec}^{-1}$ , where N is no. of molecules remaining in the container.

Q.19 Which one of the following may represent fraction of no. of molecules present after the given interval for gas-I?

(A)  $t=0$   $t=100\text{sec}$   $t=200\text{sec}$  (B)  $t=0$   $t=100\text{sec}$   $t=200\text{sec}$

1  $\frac{1}{2}$   $\frac{1}{8}$  1  $\frac{1}{8}$   $\frac{1}{16}$

(C)  $t=0$   $t=100\text{sec}$   $t=200\text{sec}$  (D)  $t=0$   $t=100\text{sec}$   $t=200\text{sec}$

1  $\frac{1}{2}$   $\frac{1}{4}$  1  $\frac{1}{4}$   $\frac{1}{16}$

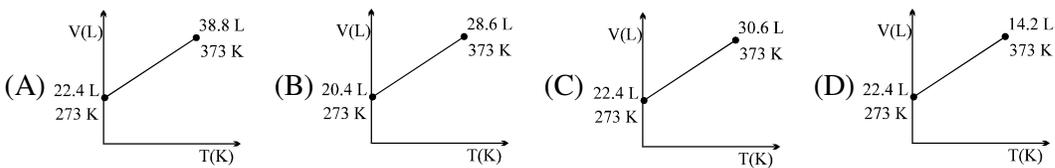
Q.20 Identify the correct option regarding sequence of (True) & (False) statements

- (i) The time required for moles of gas I to get reduced to half of original & that of gas II to reduced to half of original is independent of initial moles of gas I & gas II.
- (ii) The rate at which **initially** molecules will come out in gas I as compared to gas II will be greater in gas **II** if initial no. of molecules are same.
- (iii) The time required for moles to get reduced from 1 to 0.8 in gas I and 2 to 1.6 in gas II will be same
- (iv) For the two gases, moles remaining on the container after same interval should be in Geometrical Progression.

(A) TFFT (B) TFFT (C) FTFT (D) TTFF

### EXERCISE # IV

- Q.1 A mixture of ideal gases is cooled upto liquid He temperature (4.22 K) to form an ideal solution. Is this statement **true** or **false**. Justify your answer in not more than two lines. [JEE 1996]
- Q.2 The ratio between the r. m. s. velocity of  $H_2$  at 50 K and that of  $O_2$  at 800 K is :  
(A) 4 (B) 2 (C) 1 (D) 1/4 [JEE 1996]
- Q.3 X ml of  $H_2$  gas effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is : [JEE 1996]  
(A) 10 sec, He (B) 20 sec,  $O_2$  (C) 25 sec, CO (D) 55 sec,  $CO_2$
- Q.4 One mole of  $N_2O_4$  (g) at 300 k is kept in a closed container under one atmp. It is heated to 600 k when 20 % by mass of  $N_2O_4$  (g) decomposes to  $NO_2$  (g) . The resultant pressure is : [JEE 1996]  
(A) 1.2 atm (B) 2.4 atm (C) 2.0 atm (D) 1.0 atm
- Q.5 The absolute temperature of an ideal gas is \_\_\_\_\_ to/than the average kinetic energy of the gas molecules. [JEE 1997]
- Q.6 One way of writing the equation of state for real gases is,  
$$P \bar{V} = RT \left[ 1 + \frac{B}{\bar{V}} + \dots \right]$$
 where B is a constant.  
Derive an approximate expression for 'B' in terms of Vander Waals constant 'a' & 'b'. [JEE 1997]
- Q.7 Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6 g oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of He gas in the cylinder. Assume ideal behaviour for gases. [JEE 1997]
- Q.8 According to Graham's law, at a given temperature the ratio of the rates of diffusion  $\frac{r_A}{r_B}$  of gases A and B is given by : [JEE 1998]  
(A)  $\frac{P_A}{P_B} \left( \frac{M_A}{M_B} \right)^{1/2}$  (B)  $\left( \frac{M_A}{M_B} \right) \left( \frac{P_A}{P_B} \right)^{1/2}$  (C)  $\frac{P_A}{P_B} \left( \frac{M_B}{M_A} \right)^{1/2}$  (D)  $\frac{M_A}{M_B} \left( \frac{P_B}{P_A} \right)^{1/2}$
- Q.9 An evacuated glass vessel weighs 50.0 g when empty, 148.0 gm when filled with a liquid of density 0.98 g/mL and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 k . Determine the molecular weight of the gas . [JEE 1998]
- Q.10 Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atmp at a temperature of 300 k. The value of "b" is 0.05 litre mol<sup>-1</sup>. [JEE 1998]
- Q.11 The pressure exerted by 12 g of an ideal gas at temperature t °C in a vessel of volume V is one atmp . When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10 % . Calculate the temperature 't' and volume 'V'. [molecular weight of gas = 120] [JEE 1999]

- Q.12 One mole of  $N_2$  gas at 0.8 atm takes 38 sec to diffuse through a pin hole, whereas one mole of an unknown compound of Xenon with F at 1.6 atm takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound. (At. wt. Xe = 138, F = 19) [JEE 1999]
- Q.13 A gas will approach ideal behaviour at : [JEE 1999]  
 (A) low temperature and low pressure (B) low temperature and high pressure  
 (C) low pressure and high temperature (D) high temperature and high pressure.
- Q.14 The compressibility of a gas is less than unity at STP. Therefore [JEE 2000]  
 (A)  $V_m > 22.4$  L (B)  $V_m < 22.4$  L (C)  $V_m = 22.4$  L (D)  $V_m = 44.8$  L
- Q.15 The r. m. s. velocity of hydrogen is  $\sqrt{7}$  times the r. m. s. velocity of nitrogen. If T is the temperature of the gas : [JEE 2000]  
 (A)  $T(H_2) = T(N_2)$  (B)  $T(H_2) > T(N_2)$   
 (C)  $T(H_2) < T(N_2)$  (D)  $T(H_2) = \sqrt{7} T(N_2)$
- Q.16 The pressure of a fixed amount of an ideal gas is proportional to its temperature. Frequency of collision and their impact both increase in proportion to the square root of temperature. True/False. [JEE 2000]
- Q.17 Calculate the pressure exerted by one mole of  $CO_2$  gas at 273 K, if the Vander Waals constant  $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2}$ . Assume that the volume occupied by  $CO_2$  molecules is negligible. [JEE 2000]
- Q.18 The root mean square velocity of an ideal gas at constant pressure varies with density as [JEE 2001]  
 (A)  $d^2$  (B)  $d$  (C)  $d^{1/2}$  (D)  $1/d^{1/2}$
- Q.19 The compression factor (compressibility factor) for one mole of a vander Waals gas at  $0^\circ\text{C}$  and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the vander waals constant 'a'. [JEE 2001]
- Q.20 Which one of the following V, T plots represents the behaviour of one mole of an ideal gas at one atm?  
  
 (A)  $(273 \text{ K}, 22.4 \text{ L})$  and  $(373 \text{ K}, 38.8 \text{ L})$   
 (B)  $(273 \text{ K}, 20.4 \text{ L})$  and  $(373 \text{ K}, 28.6 \text{ L})$   
 (C)  $(273 \text{ K}, 22.4 \text{ L})$  and  $(373 \text{ K}, 30.6 \text{ L})$   
 (D)  $(273 \text{ K}, 22.4 \text{ L})$  and  $(373 \text{ K}, 14.2 \text{ L})$  [JEE 2002]
- Q.21 The density of the vapour of a substance at 1 atm pressure and 500 K is  $0.36 \text{ Kg m}^{-3}$ . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.  
 (a) Determine  
 (i) mol. wt.; (ii) molar volume; (iii) compression factor (z) of the vapour and  
 (iv) which forces among the gas molecules are dominating, the attractive or the repulsive  
 (b) If the vapour behaves ideally at 1000K, determine the average translational K.E. of a molecule. [JEE 2002]

- Q.22 The average velocity of gas molecules is 400 m/sec. Calculate its (rms) velocity at the same temperature. [JEE 2003]
- Q.23  $C_v$  value of He is always  $3R/2$  but  $C_v$  value of  $H_2$  is  $3R/2$  at low temperature and  $5R/2$  at moderate temperature and more than  $5R/2$  at higher temperature explain in two to three lines. [JEE 2003]
- Q.24 Positive deviation from ideal behaviour takes place because of [JEE 2003]

(A) molecular interaction between atoms and  $\frac{PV}{nRT} > 1$

(B) molecular interaction between atoms and  $\frac{PV}{nRT} < 1$

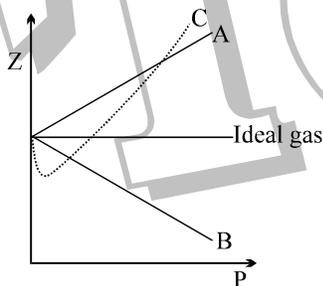
(C) finite size of atoms and  $\frac{PV}{nRT} > 1$

(D) finite size of atoms and  $\frac{PV}{nRT} < 1$

- Q.25 For a real gas obeying van der Waal's equation a graph is plotted between  $PV_m$  (y-axis) and  $P(x$ -axis) where  $V_m$  is molar volume. Find y-intercept of the graph. [JEE 2004]

- Q.26 The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be (A) 4 (B) 2 (C) 1 (D) 0.5 [JEE 2005]

Q.27



where  $Z = \frac{PV}{nRT}$ ,

a = Van der Waal's constant for pressure correction

b = Van der Waal's constant for volume correction

Pick the only incorrect statement

- (A) for gas A, if  $a = 0$ , the compressibility factor is directly proportional to pressure
- (B) for gas B, if  $b = 0$ , the compressibility factor is directly proportional to pressure
- (C) for gas C,  $a \neq 0$ ,  $b \neq 0$ , it can be used to calculate a and b by giving lowest P value and its intercept with  $Z = 1$ .
- (D) slope for all three gases at high pressure (not shown in graph) is positive. [JEE 2006]

**ANSWER KEY**  
**EXERCISE # I**

- Q.1  $P = 0.062 \text{ atm}$ ,  $T = 75 \text{ K}$       Q.2  $9.08 \text{ cm}$       Q.3  $3.8 \times 10^3 \text{ kPa}$
- Q.4  $16.07 \text{ gm}$ ;  $12 \text{ dm}^3$       Q.5  $280 \text{ ml/min}$       Q.6  $6 \text{ atm}$ , No      Q.7  $66.74 \text{ atm}$
- Q.8  $P_{\text{total}} = 27.54 \times 10^5 \text{ N/m}^2$ ,  $P_{\text{final}} = 19.66 \times 10^5 \text{ N/m}^2$       Q.9  $2.19 \text{ atmp}$       Q.10  $228$
- Q.11  $50.8 \text{ cm}$       Q.12  $16 \text{ min}$       Q.13  $\text{yes}$       Q.14  $46.6$
- Q.15 (a)  $0.33 \text{ Torr/sec}$ , (b)  $0.29 \text{ Torr/sec}$       Q.16  $0.137$       Q.18  $4.62 \times 10^3 \text{ moles}$ ,  $128.79 \text{ Kg}$ ,  $119.55 \text{ Kg}$
- Q.19  $25.027 \text{ KPa}$       Q.20  $71.4 \text{ L}$       Q.21  $2.53^\circ\text{C}$       Q.22  $\text{yes}$
- Q.23  $175.133 \text{ kg mol}^{-1}$       Q.24  $32.14 \text{ g/mol}$ ,  $460.28 \text{ m/s}$       Q.25  $236.3^\circ\text{C}$
- Q.26  $183,800 \text{ cm/sec}$       Q.27  $8.88 \times 10^5 \text{ (m/s)}^2$ ;  $71.27 \text{ K}$
- Q.28  $6.06 \times 10^{23} \text{ molecules mol}^{-1}$       Q.29  $U_{\text{RMS}} = 493 \text{ m/s}$ ,  $U_{\text{mp}} = 403 \text{ m/s}$ ,  $U_{\text{av}} = 454.4 \text{ m/s}$
- Q.30  $280 \text{ K}$ ,  $525 \text{ K}$ ,  $3.157 \times 10^2 \text{ m/sec}$ ,  $2.798 \times 10^2 \text{ m/sec}$
- Q.31  $T_{\text{RMS}} = 2886 \text{ K}$ ,  $T_{\text{av}} = 3399 \text{ K}$ ,  $T_{\text{mp}} = 4330 \text{ K}$       Q.32  $8.303 \times 10^{-3}$
- Q.33  $0.199$       Q.34  $A$       Q.35  $3.3 \times 10^3 \text{ cm}$
- Q.36  $314 \text{ pm}$ ,  $7.015 \text{ cm}$ ,  $6742 \text{ s}^{-1}$ ,  $1.09 \times 10^{17} \text{ cm}^{-3} \text{ s}^{-1}$       Q.37  $\text{He}$
- Q.38 (a)  $1.281 \times 10^{23} \text{ m}^{-3}$ , (b)  $5.306 \times 10^2 \text{ Pa}$       Q.39  $58.997 \text{ cm}^3$
- Q.40 (a)  $2.479 \times 10^3 \text{ kPa}$ , (b)  $2225.55 \text{ kPa}$       Q.41  $3.77 \text{ L}$       Q.42  $15.40 \text{ kg}$
- Q.43  $521 \text{ K}$       Q.44 (i) B, (ii) C, (iii) A      Q.45  $4500 \text{ RJ}$       Q.46  $\pi = 2.99$ ,  $\theta = 1.90$
- Q.48  $350.5^\circ\text{C}$       Q.49 (i)  $31.1 \text{ atm}$ , (ii)  $31.4 \text{ atm}$       Q.50  $r = 1.33 \times 10^{-8}$
- Q.51  $\text{Molar vol} = 0.1353 \text{ L/mol}$ ;  $Z = 0.6957$
- Q.52 (a)  $2.52 \times 10^{-3} \text{ l mol}^{-1}$ , (b)  $10.08 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$

**EXERCISE # II**

- Q.1  $4 : 7 : 5$       Q.2  $14.41 \text{ m}^3$       Q.3  $\frac{2\sqrt{2}}{3\sqrt{\pi}} Z_1$
- Q.4  $10 \text{ Steps}$ ,  $27.78 \text{ mol CH}_4$ ,  $5333.3 \text{ mol O}_2$       Q.5(a)  $0.625$ , (b)  $4$       Q.6  $2.2 \text{ g}$
- Q.7  $T_1 = 300 \text{ K}$ ,  $T_2 = 900 \text{ K}$       Q.8  $13$       Q.9  $2 \text{ atmp}$

- Q.10 (a) 1.257 L; (b) At 383 K  $P_T = 113.99$  kpa ,  $P_{O_2} = 38$  kpa ,  $P_{CO} = 25.33$  kpa ,  $P_{H_2O} = 50.66$  kpa ,  
At 283 K  $P_T = 46.81$  kpa ,  $P_{O_2} = 28.086$  kpa ,  $P_{CO} = 18.724$  kpa ,  $P_{H_2O} = 0$   
(c) Before reaction :  $CH_4 = 0.01 N_A$  ,  $O_2 = 0.03 N_A$   
After reaction :  $O_2 = 0.015 N_A$  ,  $CO = 0.01 N_A$  ,  $H_2O = 0.02 N_A$

Q.11 421.9 K

- Q.12 (i) 5.263 L, (ii) 0.7 Kg/m<sup>3</sup>, (iii)  $K_{OH} = 0.2348$  moles,  $Ca(OH)_2 = 0.1174$  moles, ethanolamine = 0.2348 moles

Q.13 10,000 K

$$Q.14 \quad n = \frac{-T}{100} + 5, \quad V = \frac{-RT^2}{100} + 5RT, \quad 51.3125 \text{ l}$$

$$Q.15 \quad V_C = \frac{6B}{A}, T_C = \frac{A^2}{6RB}, P_C = \frac{A^3}{108B^2}, \text{ compressibility factor} = \frac{P_C V_C}{RT_C} = \frac{1}{3} \quad Q.16 \quad 0.825 \text{ L}$$

### EXERCISE # III

- Q.1 B    Q.2 B    Q.3 B    Q.4 D    Q.5 C    Q.6 A    Q.7 B  
Q.8 D    Q.9 A    Q.10 C    Q.11 C    Q.12 B    Q.13 A    Q.14 C  
Q.15 C    Q.16 A    Q.17 C    Q.18 B    Q.19 C    Q.20 A

### EXERCISE # IV

- Q.1 yes it is false statement    Q.2 C    Q.3 B    Q.4 B    Q.5 directly proportional  
Q.6  $B = \left( b - \frac{\alpha}{RT} \right)$     Q.7 0.492 atmp ; 0.246 atmp    Q.8 C    Q.9 123  
Q.10 6.46 atmp L<sup>2</sup> mol<sup>-2</sup>    Q.11 -173°C , 0.82 L    Q.12 XeF<sub>6</sub>    Q.13 C  
Q.14 B    Q.15 C    Q.16 Both statements are correct    Q.17 34.8 atmp  
Q.18 D    Q.19 1.2544 atmp L<sup>2</sup> mol<sup>-2</sup>    Q.20 C  
Q.21 (a) (i) 18.1 g/mol , (ii) 50.25 L mol<sup>-1</sup> , (iii) 1.224 , (iv) repulsive, (b)  $2.07 \times 10^{-20}$  J  
Q.22 434.17 m/sec  
Q.23 Since H<sub>2</sub> is diatomic and He is monoatomic degree of freedom for mono is 3 and only translational but for diatomic, vibrational and rotational are also to be considered  
Q.24 C    Q.25 RT    Q.26 B    Q.27 C