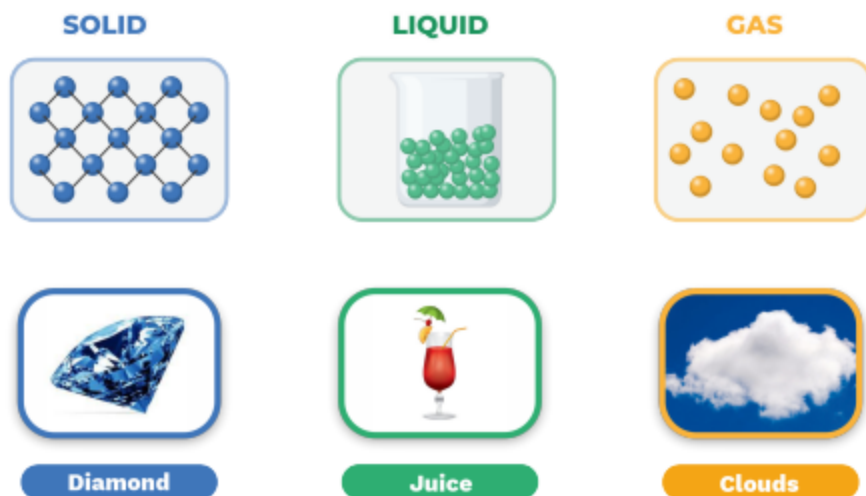


# States of Matter

## STATES OF MATTER



### Comparison of solids, liquids and gases ::

S.no	Property	Gaseous state	Liquid state	Solid state
1	General	It has definite mass but no definite shape and volume	It has definite mass and volume but no definite shape	It has definite mass, volume and shape
2	Forces	Almost negligible	Weaker than those in solids	Strongest
3	Density	Lowest	Lower than solids	Highest
4	Motion	Molecules have large rotatory, vibratory and translatory motions	Molecules have vibratory and translatory motion	No translatory or rotatory motion. Possess vibratory motion
5	Packing	No proper packing	Less closely packed	Molecules closely packed
6	Kinetic Energy	Highest	Moderate	Negligible
7	Thermal Expansion	Highest	Higher than solid	Least

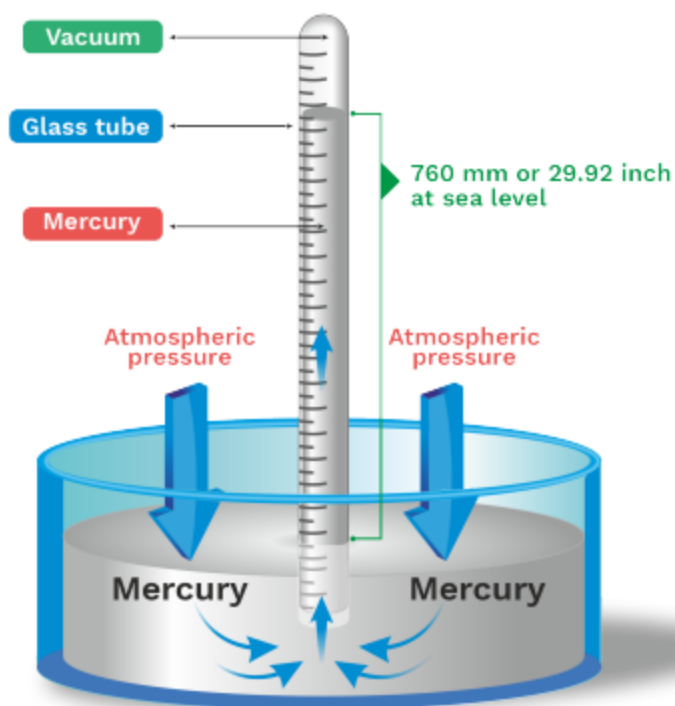


S.no	Property	Gaseous state	Liquid state	Solid state
8	Compression	Highest	Slightly higher than solid	Least compressible
9	Intermixing	Spontaneous	Spontaneous but slow	Intermixing is least
10	Pressure	Exert pressure on the walls of container	Negligible	Negligible

### Instruments for pressure Calculations :

#### Pressure :

Pressure of a gas is defined as the force exerted by the gas on unit area of the walls of vessel. It is often observed that pressure is isotropic i.e it is the same in all the three directions.



#### Rack your Brain



Atmospheric pressure is measured at sea level. What is the reason behind this?

#### Concept Ladder



Any gaseous state is characterized by sensitivity of volume change with change of pressure and temperature.



$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

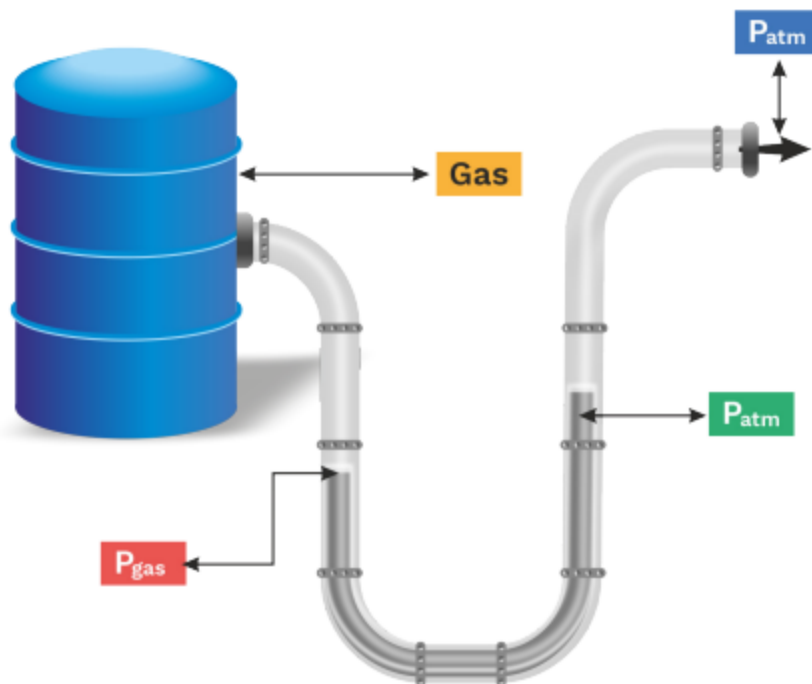
$$P = \frac{Mg}{A} = \frac{V \times \rho \times g}{A}$$

**Barometer :**

$$\text{Pressure} = \frac{A \times h \times \rho \times g}{A}, \quad [A = \text{Area}]$$

**Manometer :**

$$P_{\text{gas}} = P_{\text{atm}} + h\rho g$$



where,

$\rho$  = density of fluid

$h$  = vertical height

$g$  = acceleration due to gravity

**Gas law :**

**Experimental Gas laws**

It is the only state that allows a quantitative relationship between the four variables,  $P$ ,  $V$ ,  $T$  &  $n$ . The relationship which connects the four variables is known as equation of state, which can be obtained experimentally from the following gas laws.

**Rack your Brain**



Does the volume of solid and liquid depend on pressure?

**Concept Ladder**

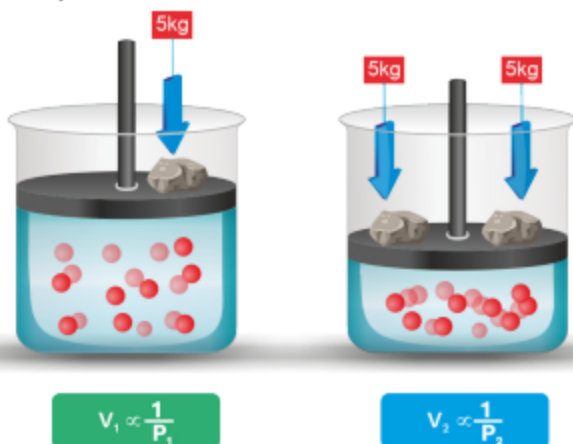


The gases following these laws generally exist at lower value of pressure.



- **Boyle's law :**

Pressure (P) of a given mass of gas varies inversely to its volume (V), at constant temperature.



- $P \propto \frac{1}{V}$  [T, being constant]

$$PV = K$$

Where K is a proportionally constant

- $\log P + \log V = \text{constant}$

$$P_1V_1 = P_2V_2$$

**Applications of Boyle's Law:**

- Storage of gas,
- Scuba diving or deep water diving
- The mechanics of human breathing
- Spray Paint
- Working of syringe

**Rack your Brain**



Air at sea level is dense. This is a practical application of which law?



**Previous Year's Questions**

At 25°C and 730 mm pressure, 380 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure?

[AIPMT]

- (1) 569 mL      (2) 365 mL  
(3) 265 mL      (4) 621 mL

**Q1**

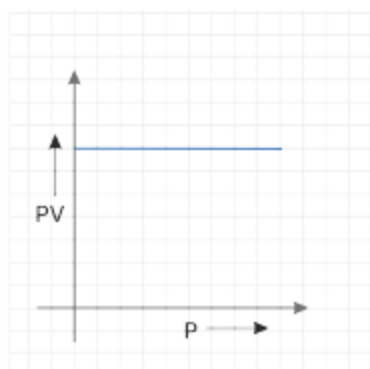
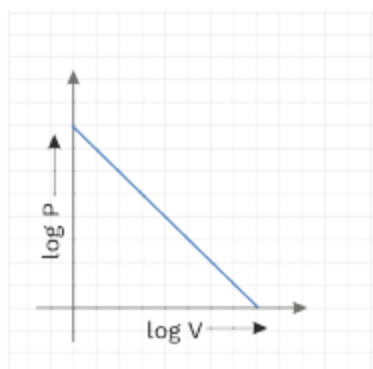
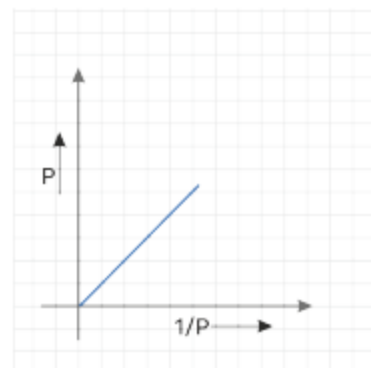
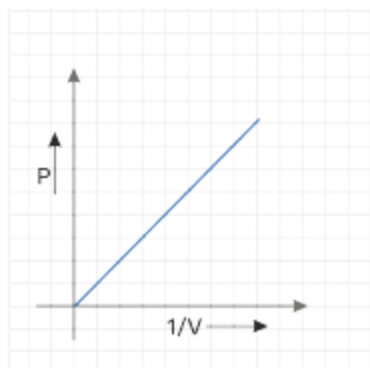
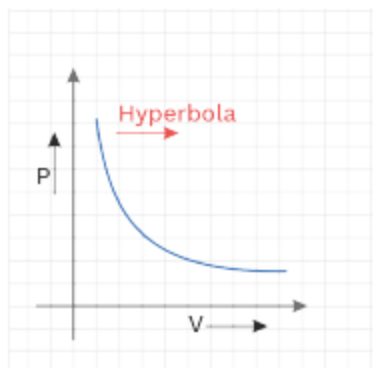
What is the volume of a sample of oxygen at a pressure of 3.5 bar if its volume at 1 bar is 3.15 L at the same temperature?

**Sol.**

Here,  $P_1 = 1$  bar,  $P_2 = 3.5$  bar,  $V_1 = 3.15$  L,  $V_2 = ?$

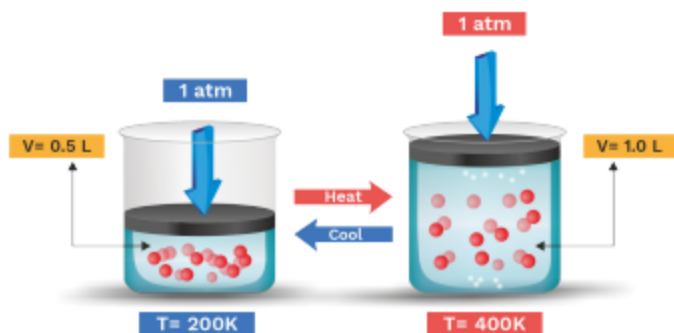
From Boyle's law equation  $P_1V_1 = P_2V_2$ , we get

$$V_2 = \frac{P_1V_1}{P_2} = \frac{1.00 \text{ bar} \times 3.15 \text{ L}}{3.5 \text{ bar}} = 0.90 \text{ L}$$



## 2. Charles's Law :

At constant pressure, the volume ( $V$ ) of a given mass of gas varies directly as the absolute temperature ( $T$ )



Means :  $V \propto T$

[Pressure = constant,  $V$  = Volume,  $T$  = Temperature]

## Previous Year's Questions



Pressure remaining the same, the volume of a given mass of an ideal gas increases for every degree centigrade rise in temperature by definite fraction of its volume at

[AIPMT]

- (1)  $0^\circ\text{C}$
- (2) its critical temperature
- (3) absolute zero
- (4) its Boyle temperature



$$V = KT \quad \text{OR} \quad \frac{V}{T} = K; \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

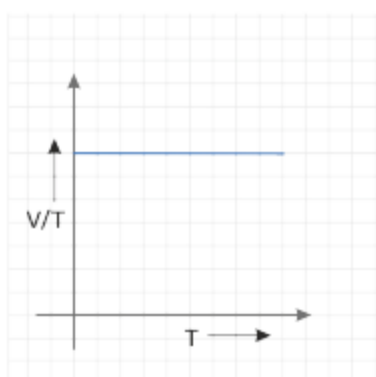
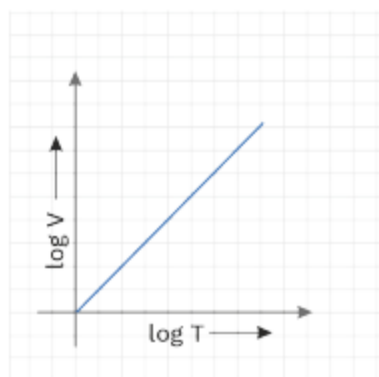
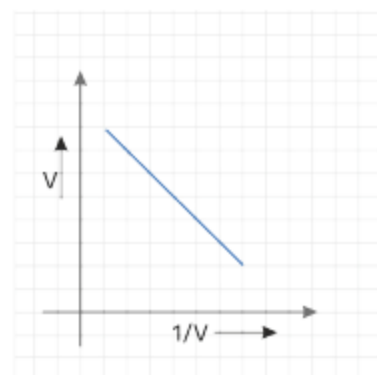
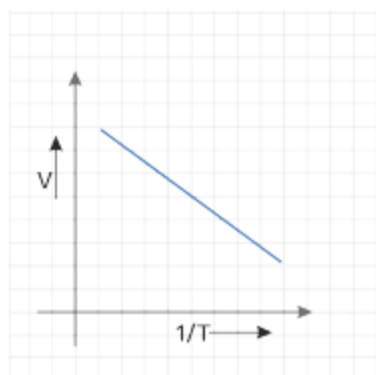
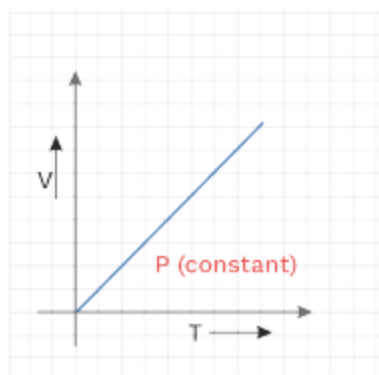
### Applications of Charle's Laws:

- Overfilling of tube can swell up in the sun and burst.
- A hot air balloon
- Turkey Thermometer.
- Car engine.

### Concept Ladder



The volume of a fixed mass of gas changes by  $1/273$  of its volume at  $0^\circ\text{C}$  for each degree rise or fall of temperature, when  $P$  is constant.



### 3. Gay Lussac's law :

At constant volume the pressure ( $P$ ) of given mass of gas varies directly to the absolute temperature ( $T$ ).

Means  $P \propto T$  (Volume = constant)

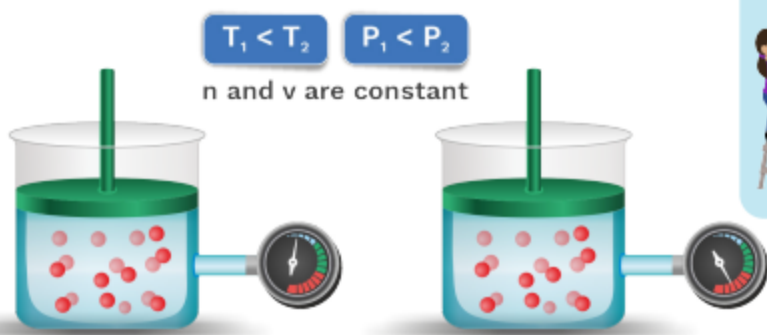
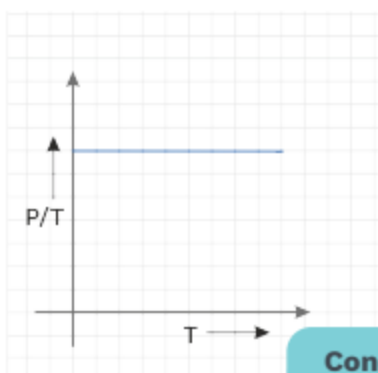
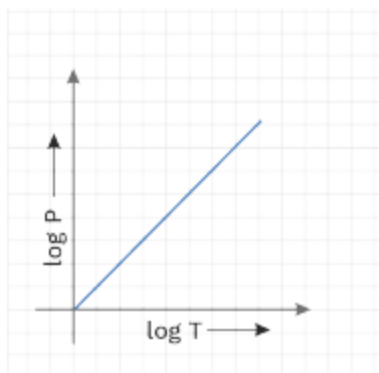
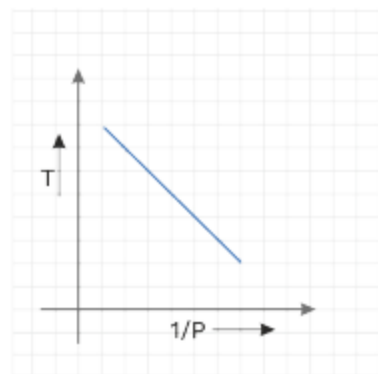
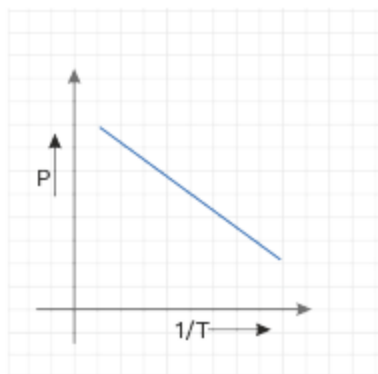
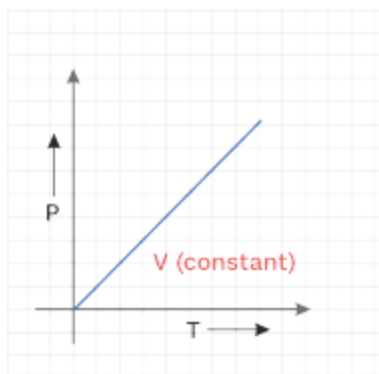
$$\text{OR} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\text{OR} \quad \log P - \log T = \text{Constant}$$

### Rack your Brain



Use of hot air balloons in sports and meteorological observations is an application of which law ?



### Concept Ladder



The plot of pressure versus temperature (K) for a fixed mass of gas at constant volume is a straight line.

### Ideal gas Equation :

This equation combines both the Boyle's and Charles's law

According to Boyle's law

$$V \propto \frac{1}{P} \quad (\text{at constant } T)$$

### Definitions

The gas which obeys the equation  $PV = nRT$  at every temperature and pressure range strictly is known as ideal gas.



According to Charles's law

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

OR combine :  $V \propto \frac{T}{P}$

OR  $PV \propto T$  [ $PV = RT$  for 1 mole]

OR  $\frac{PV}{T} = \text{constant (R)}$

For n moles,

$$PV = nRT$$

### Universal Gas constant (R)

$$= 0.0821 \frac{\text{atm.litre}}{\text{mol.K}} = 8.314 \times 10^7 \frac{\text{erg}}{\text{mol.K}}$$

$$= 8.314 \frac{\text{J}}{\text{mol.K}} = 1.99 \frac{\text{Cal.}}{\text{mol.K}}$$

In case of two different conditions :

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

### Important results :

At 0°C,  $RT = 0.0821 \times 273 = 22.4 \text{ L}$

At 27°C,  $RT = 0.0821 \times 300 = 24.6 \text{ L}$

### Given standard condition

Volume of 1 mole = 22.4 litre

0° C temperature = 273 K

1 atmospheric pressure = 760 mm of Hg

i.e known as STP or NTP

### Application of Ideal gas equation

- Calculation of mass and molecular weight of the Gas
- $PV = nRT$

$$P = \frac{n}{V} RT$$

$$P = CRT$$

- $n = \frac{m}{M} = \text{Weight in gm of gas} / \text{Gram molecular weight}$   
 $PV = \frac{m}{M} RT$

### Rack your Brain



An ideal gas is one which obeys the gas laws under which condition?

### Concept Ladder



A gas behaves as an ideal gas at very low pressure and very high temperature as the molecules are very far from each other.

### Previous Year's Questions



Select one correct statement. In the gas equation,  $PV = nRT$

[AIPMT]

- (1) n is the number of molecules of a gas
- (2) V denotes volume of one mole of the gas
- (3) n moles of the gas have a volume V
- (4) P is the pressure of the gas when only one mole of gas is present





• **Calculation of density (d) of gas**

$$PV = \frac{m}{M}RT$$

$$P = \frac{m}{V} \times \frac{RT}{M} = \frac{dRT}{M}$$

$$\frac{dT}{P} = \frac{M}{R} \quad \frac{M}{R} = \text{constant}$$

So, also for the different temperature and pressure

$$\frac{d_1 T_1}{P_1} = \frac{d_2 T_2}{P_2} \quad [d = \text{density of gas}]$$



**Previous Year's Questions**

If P, V, M, T and R are pressure, volume, molar mass, temperature and gas constant respectively, then for an ideal gas, the density is given by

- (1)  $\frac{RT}{PM}$                       (2)  $\frac{P}{RT}$                       [AIPMT]  
 (3)  $\frac{M}{V}$                               (4)  $\frac{PM}{RT}$

- Q2** A football has a volume of 8 litre when filled with air on a day when the atmospheric pressure is 720 torr. What volume will the football occupy when the pressure has increased to 760 torr ?  
 (1) 8.75 litre    (2) 5.58 litre    (3) 7.58 litre    (4) 10.75 litre

**Sol.** (3)  
 Using Boyle's law    [ $P_1 V_1 =$  initial pressure and initial volume]  
 $P_1 V_1 = P_2 V_2$                       [ $P_2 V_2 =$  final pressure and final volume ]  
 $P_1 = 720$  torr  
 $P_2 = 760$  torr  
 $V_1 = 8$  litre  
 $V_2 = ?$   
 So,     $720 \times 8 = 760 \times V_2$   
 $V_2 = \frac{720 \times 8}{760} = 7.58$  litre

- Q3** A bicycle tyre is filled with 3.0 litre of air when the surrounding air temperature is 27°C. What will be the volume of air in the tyre the next morning when the temperature is 17°C ?  
 (1) 9.2 litre                      (2) 2.9 litre                      (3) 5.9 litre                      (4) 4.9 litre

**Sol.** (2)

According to Charle's law  $[V \propto T]$

$$\text{Given, } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 3.0 \text{ litre ; } V_2 = ?$$

$$T_1 = 273 + 27 = 300 \text{ K}$$

$$T_2 = 273 + 17 = 290 \text{ K}$$

$$V_2 = \frac{3 \times 290}{300} = 2.9 \text{ litre}$$

**Q4**

Under normal driving condition a car was found to emit 3.8 litre of nitric oxide (NO) per hour, measured at 750 torr and 27°C. What volume would be emitted per hour under STP condition ?

(1) 6.243 litre

(2) 2.275 litre

(3) 1.175 litre

(4) 3.413 litre

**Sol.** (4)

$$P_1 = 760 \text{ torr ; } P_2 = 750 \text{ torr}$$

$$V_1 = ? ; V_2 = 3.8 \text{ litre}$$

$$T_1 = 273 \text{ K ; } T_2 = 273 + 27 = 300 \text{ K}$$

So, according to ideal gas equation

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

$$\frac{760 \times V_1}{273} = \frac{750 \times 3.8}{300}$$

$$V_1 = 3.413 \text{ litre}$$

**Q5**

A sample of gas occupies a volume of 320 cm<sup>3</sup> at STP. Calculate its volume at 66°C and 0.825 atm pressure.

**Sol.** Here,  $P_1 = 1.00 \text{ atm}$ ,  $P_2 = 0.825 \text{ atm}$ ,  $V_1 = 320 \text{ cm}^3$ ,  $V_2 = ?$

$$T_1 = 273 \text{ K}, T_2 = 66^\circ\text{C} = (66 + 273) \text{ K} = 339 \text{ K}$$

According to the gas equation,

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

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{1 \times 320 \times 339}{273 \times 0.825} = 482 \text{ cm}^3$$

**Important conversions :**

Parameters	Unit Conversions
Pressure	1 atm = $1.0132 \times 10^5$ Pa = 760 mm of Hg = 760 torr = 1.013 bar
Volume	1 l = $1 \text{ dm}^3 = 10^{-3} \text{ m}^3$ = 1000 ml = $1000 \text{ cm}^3$
Temperature	$T_k = T_c + 273.15$

- Q6** Calculate density of  $\text{SO}_2$  at  $25^\circ\text{C}$  and 770 torr  
 (1) 5.65 g/lit                      (2) 8.25 g/lit                      (3) 4.85 g/lit                      (4) 2.65 g/lit

**Sol.** (4)  
 Gram mol weight of  $\text{SO}_2 = 64$

As we know,  $PM = dRT$                       [1 torr = 1 mm of Hg]

$$d = \frac{M}{R} \times \frac{P}{T} \quad [1 \text{ atm} = 760 \text{ mm of Hg}]$$

$$= \frac{64 \times 770}{760} \times \frac{1}{0.082} \times \frac{1}{298} = 2.65 \text{ g/lit}$$

- Q7** Boyle's law may be expressed as :  
 (1)  $\left(\frac{dP}{dV}\right)_T = \frac{K}{V}$                       (2)  $\left(\frac{dP}{dV}\right)_T = \frac{K}{V^2}$                       (3)  $\left(\frac{dP}{dV}\right)_T = \frac{-K}{V}$                       (4) None

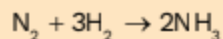
**Sol.** (2)  
 $PV = \text{constant}$   
 $PdV + Vdp = 0$

$$\text{Or } \frac{dP}{dV} = \left(\frac{-P}{V}\right)_T$$

$$\Rightarrow \frac{dP}{P} = -\frac{dV}{V} = \frac{-K}{V^2}$$



**Q8** 2 mol  $N_2$  and 3 mol  $H_2$  gas are allowed to react in a 20 litre flask at 400 K and after complete conversion of  $H_2$  into  $NH_3$ , 10L  $H_2O$  was added and temperature reduced to 300 K pressure of the gas after reaction is :



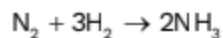
(1)  $3R \times \frac{300}{20}$

(2)  $3R \times \frac{300}{10}$

(3)  $R \times \frac{300}{20}$

(4)  $R \times \frac{300}{10}$

**Sol.** (4)



$$2 \quad 3 \quad 0$$

$$2-x \quad 3-3x \quad 2x$$

Limiting reagent is  $H_2$ , so  $x = 1$

$$1 \quad 0 \quad 2 \text{ mol}$$

On adding 10 litre water, volume of flask will remain 10 litre for gases

$$PV = nRT$$

$$P \times 10 = 1 \times R \times 300$$

$$\text{So, } P = \frac{R \times 300}{10}$$

**Q9** The constant R is :

(1) Work done per molecule

(2) Work done per degree absolute

(3) Work done per degree per mole

(4) Work done per mole

**Sol.** (3)

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{W}{1 \times 1}$$

**Q10** In a container  $m$  gm of a gas is placed. After some time some gas is allowed to escape from container. The pressure of the gas becomes half and its absolute temperature  $2/3^{\text{rd}}$ . The amount of the gas escaped is :

(1)  $\frac{2}{3} m$

(2)  $\frac{1}{2} m$

(3)  $\frac{1}{4} m$

(4)  $\frac{1}{6} m$



**Sol.** (3)

$$PV = \frac{w}{m}RT$$

$$P \propto wT$$

$$P_1 = P, P_2 = \frac{P}{2}, T_1 = T, T_2 = \frac{2}{3}T$$

$$\frac{P}{P/2} = \frac{m \times T}{w_2 \times \frac{2}{3}T}$$

$$w_2 = \frac{3}{4}m$$

$$\text{So, amount of gas escaped} = m - \frac{3}{4}m = \frac{m}{4}$$

**Q11** 4 gm of argon (at mass = 40) in a bulb at a temperature of T K had a pressure P atm. When the bulb was placed in hotter bath at a temperature 50° more than first one, 0.8 gm of gas had to be removed to get the original pressure. T is equal to :

(1) 510 K

(2) 200 K

(3) 100 K

(4) 73 K

**Sol.** (2)

$$m_1 T_1 = m_2 T_2$$

$$4 \times T = 3.2 (T+50)$$

$$4T = 3.2T + 160$$

$$0.8T = 160$$

$$T = \frac{1600}{8} = 200K$$

**Q12** A glass bulb is connected to an open limb manometer. The level of mercury in both limbs of the manometer was same. The bulb was heated to 57°C. If the room temperature and the atmospheric pressure were 27°C and 750 mm. The difference of levels in the two limbs now will be :

(1) 2.5 cm

(2) 5.0 cm

(3) 7.5 cm

(4) 10.0 cm

**Sol.** (3)

$$\frac{75}{300} = \frac{P_2}{330} \Rightarrow P_2 = \frac{75 \times 330}{300} = 82.5$$

∴ difference = 7.5 cm

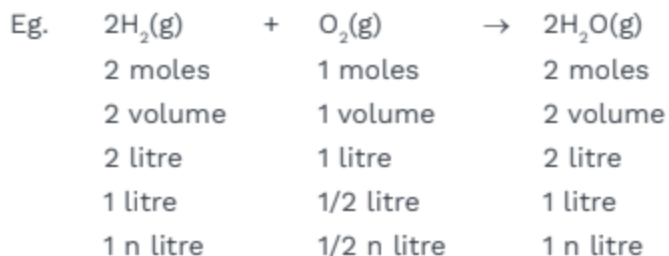
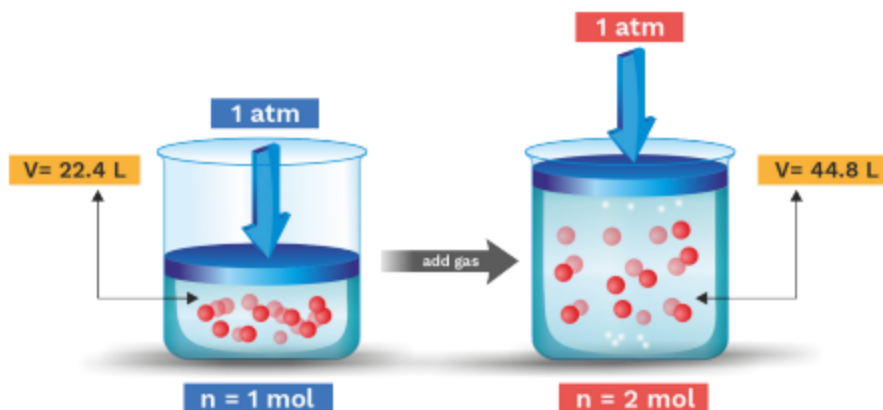


### 5. Avogadro's law :

This states that equal volumes of gases under similar conditions of pressure and temperature possess equal number of moles.

$$V \propto n \quad \text{at constant P and T}$$

Where, n is the total number of moles in volume V



### Amagat's Law :

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

This is the experimental expression of volume as extensive quantity. It is named after Emile Amagat.

Both Amagat's and Dalton's laws predict the properties of gas mixtures.

### Rack your Brain



Can you guess what is the effect of increasing pressure in case of gaseous reactant ?



### Previous Year's Questions

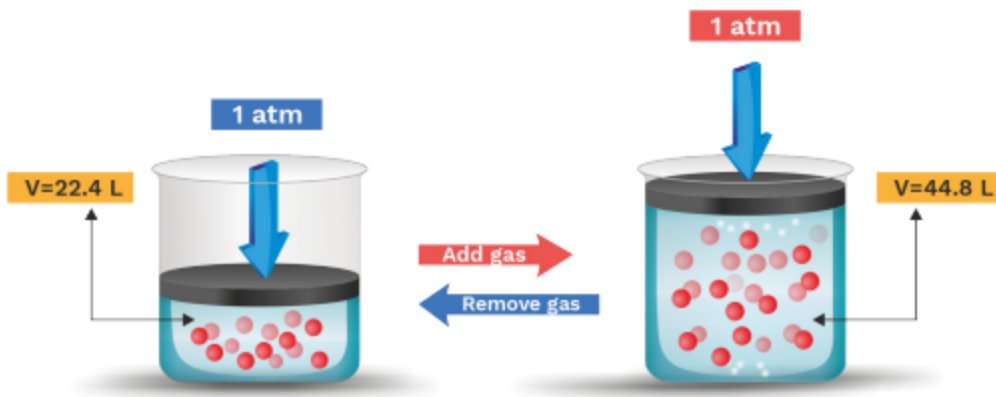
The volume occupied by 1.8 g of water vapour at  $374^\circ\text{C}$  and 1 bar pressure will be : **[NEET-2019]**

- (1) 96.66L      (2) 55.87 L  
(3) 3.10 L      (4) 5.37 L

### Rack your Brain



Which law relates volume directly with moles?



# P V T Gas Laws

**Boyle's Law**

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

As water bubble rises its size increases because pressure decreases.

**Charles's Law**

$V \propto T$

As temperature increases, volume increases.

**$PV = nRT$**

As number of moles increase, volume increases

**Avogadro's Law**

$V \propto n$

As temperature increases pressure inside the container increases and it explodes

**Gay Lussac's Law**

$T \propto P$

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

The law of states that the total pressure exerted by a mixture of non-reacting gases is equal to sum of the partial pressure exerted by the individual gases.

$$P = P_1 + P_2 + P_3 + \dots$$

$$P_{\text{Moist vapour}} = P_{\text{Dry gas}} + P_{\text{vapour}}$$

$$P_{\text{Dry gas}} = P_{\text{Moist vapour}} - \text{Aq. Tension}(p_{\text{H}_2\text{O}})$$

**Calculation of Partial Pressure :**

1. In form of ideal gas equation :

$$P_A V = n_A RT$$

$$P_B V = n_B RT$$

$$P = P_A + P_B$$

2.  $P_A = X_A \times P$

$$P_B = X_B \times P$$

**Relationship between total pressure and individual pressure of the constituent gases at constant pressure**

$$\therefore \text{Total volume} = V_1 + V_2$$

$$\therefore P_A (V_1 + V_2) = P_1 V_1$$

$$\therefore P_A = \frac{V_1}{(V_1 + V_2)} \times P_1 ; P_B = \frac{V_2}{(V_1 + V_2)} \times P_2$$

**Application of Dalton's law**

Gases are generally collected over water.

The gas collected over water also has water vapour. The pressure of the water vapour is constant at a particular temperature and is known as aqueous tension at that temperature.  $P_{\text{observed}} = P_{\text{gas}} + \text{Aqueous tension}$

$$\therefore P_{\text{gas}} = P_{\text{observed}} - \text{Aqueous tension}$$

The aqueous tension of water at different temperatures is different.

**Previous Year's Questions**

A gaseous mixture was prepared by taking equal moles of CO and  $N_2$ . If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen ( $N_2$ ) in the mixture is

[AIPMT-2011]

- (1) 0.5 atm                      (2) 0.8 atm  
(3) 0.9 atm                      (4) 1 atm

**Definitions**

The pressure exerted by the individual gases is called partial pressure.

**Previous Year's Questions**

A mixture of  $N_2$  and Ar gases in a cylinder contains 7 g of  $N_2$  and 8g of Ar. If the total pressure of the mixture of the gases in the cylinder is 27 bar the partial pressure of  $N_2$  is :

[NEET-2020]

- (1) 9 bar                              (2) 12 bar  
(3) 15 bar                              (4) 18 bar





**Q13** Calculate the total pressure in a gaseous mixture containing 16 grams of oxygen and 2 grams of hydrogen. The mixture is contained in a 22.4 litre vessel at 27°C.

(1) 1 atm

(2) 1.6 atm

(3) 2.4 atm

(4) 2 atm

**Sol.**

(2)

Number of moles of oxygen  $n_1 = \frac{16}{32} = 0.5$  moles

So, partial pressure,  $P_1 V_1 = n_1 RT$

$$P_1 = \frac{0.5 \times 0.082 \times 300}{22.4} = 0.549 \text{ atm}$$

Similarly number of moles of hydrogen  $H_2 = \frac{2}{2} = 1$

So, partial pressure

$$P_2 = \frac{1 \times 0.082 \times 300}{22.4} = 1.098 \text{ atm}$$

So, total pressure  $P = P_1 + P_2 = 1.098 + 0.549 = 1.647$  atm

**Q14** 500 ml of nitrogen at a pressure of 700 mm of Hg and 600 ml of oxygen at 800 mm of Hg are passed into a 2 litre flask at the same temperature. Calculate the total pressure of the mixture of gases :

(1) 825 mm of Hg

(2) 615 mm of Hg

(3) 365 mm of Hg

(4) 415 mm of Hg

**Sol.**

(4)

From Boyle's law.

$$P_1 V_1 = P_{N_2} V_2$$

$$P_2 \times 2000 = 500 \times 700$$

$$P_{N_2} = 175 \text{ mm of Hg}$$

$$P_{O_2} = \frac{600 \times 800}{2000} = 240 \text{ mm of Hg}$$

So, total pressure = 175 + 240 = 415 mm of Hg



- Q15** A vessel has nitrogen gas and water vapour at a total pressure of 1 atm. The partial pressure of water vapour is 0.3 atm. The contents of this vessel are transferred to another vessel having one third of the capacity of original volume, completely at the same temperature, the total pressure of the system in the new vessel is :
- (1) 3.0 atm    (2) 1 atm    (3) 3.33 atm    (4) 2.4 atm

**Sol.** (4)  
 $P_{\text{dry air}} = 1 - 0.3 = 0.7$   
If volume is one third then pressure = 2.1  
Then  $P_{\text{moist air}} = 2.1 + 0.3 = 2.4 \text{ atm}$

- Q16** Equal masses of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is :
- (1)  $\frac{1}{2}$                       (2)  $\frac{8}{9}$                       (3)  $\frac{1}{9}$                       (4)  $\frac{16}{17}$

**Sol.** (2)

$$\frac{\text{CH}_4}{\frac{m}{16}} + \frac{\text{H}_2}{\frac{m}{2}}$$
$$\frac{m + 8m}{16} = \frac{9m}{16}$$
$$\therefore P_{\text{H}_2} = \frac{m}{2} \times \frac{16}{9m} = \frac{8}{9}$$

- Q17** Atmospheric air contains 20% O<sub>2</sub> and 80% N<sub>2</sub> by volume and exerts a pressure of 760 mm. Calculate the partial pressure of O<sub>2</sub> and N<sub>2</sub> gas :
- (1) 152 mm, 608 mm                      (2) 608 mm, 152 mm  
(3) 425 mm, 335 mm                      (4) 335 mm, 425 mm

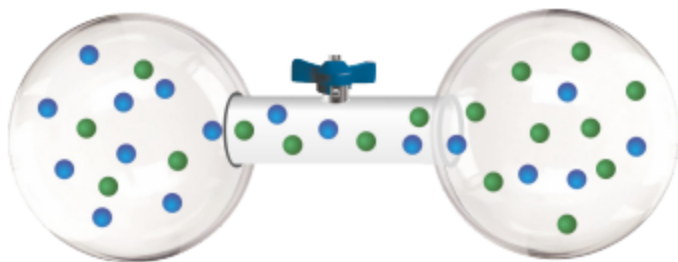
**Sol.** (1)  
Partial pressure = volume fraction × total pressure  
 $P_{\text{O}_2} = \frac{20}{100} \times 760 = 152 \text{ mm}$   
 $P_{\text{N}_2} = 0.8 \times 760 = 608 \text{ mm}$



**Q18** Two flask of equal volume connected by a narrow tube (of negligible volume) are at  $27^\circ\text{C}$  and contain 0.70 mole of  $\text{H}_2$  at 0.5 atm. One of the flask is then immersed into a bath kept at  $127^\circ\text{C}$ , while the other remain at  $27^\circ\text{C}$ . Calculate the number of mole of  $\text{H}_2$  in each flask

- (1) 0.35 mol, 0.35 mol                      (2) 0.4 mol, 0.3 mol  
 (3) 0.5 mol, 0.2 mol                        (4) 0.6 mol, 0.1 mol

**Sol.** (2)



Two flask initially at  $27^\circ$  and 0.5 atm have same volume and 0.7 mole means each has 0.35 mole

Let on heating II at  $127^\circ\text{C}$  n mole of gas are diffused from II to I.

$$\therefore \text{mole in I flask} = (0.35 + n)$$

$$\text{mole in II flask} = (0.35 - n)$$

$$\text{For I } P_{\text{New}} \times V = (0.35 + n) \times R \times 300$$

$$\text{For II } P_{\text{New}} \times V = (0.35 - n) \times R \times 400$$

$$\therefore n = 0.05$$

$$\text{Moles in flask I} = 0.35 + 0.05 = 0.40$$

$$\text{Moles in flask II} = 0.35 - 0.05 = 0.30$$

**Q19** Why dry air is heavier than moist air?

**Sol.** Average molecular weight of dry air is  $= \frac{\% \text{ of } \text{N}_2 \times 28 + \% \text{ of } \text{O}_2 \times 32}{100}$

$$\text{Average molecular weight of moist air is} = \frac{\% \text{ of } \text{N}_2 \times 28 + \% \text{ of } \text{O}_2 \times 32 + \% \text{ of } \text{H}_2\text{O} \times 18}{100}$$

Average molecular weight of dry air is more than moist air and hence its density ( $d = M/V$ ).

**Graham's law of diffusion**

The law states that at constant temperature (T) and pressure (P), the rate of diffusion of gases is inversely proportional to the square root of their densities.

$$r \propto \frac{1}{\sqrt{d}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Where  $r_1$  and  $r_2$  are rate of diffusion and  $d_1$  and  $d_2$  are vapour densities.

**Graham's law can be modified in following ways :**

1. As we know,

$$\text{Mol. Wt} = 2 \times \text{V.D}$$

$$\Rightarrow \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$\sqrt{\frac{M_2}{M_1}}$  is known as enrichment factor

$$\text{Rate of diffusion} = \frac{\text{Vol. of gas diffused}}{\text{time taken for diffusion}} = \frac{V}{t}$$

$$\text{So, } r_1 = \frac{V_1}{t_1} \text{ and } r_2 = \frac{V_2}{t_2}$$

2. When volume diffused is equal in two gases, the relationship is modified to  $\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$  and

when time diffusion is same, the equation is modified to  $\frac{V_1}{V_2} = \sqrt{\frac{M_2}{M_1}}$ . Further, rate of

diffusion ( $r$ )  $\propto \frac{P}{\sqrt{M}}$  at constant temperature.

Hence  $\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$  at constant temperature.

The Graham's relation can be also written as

$$\frac{n_1}{n_2} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{w_1}{M_1} \times \frac{M_2}{w_2} = \sqrt{\frac{M_2}{M_1}}$$

**Definitions**

The intermixing of different states of matter is known as diffusion.

**Concept Ladder**

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 remains constant.

**Previous Year's Questions**

Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape ?

[NEET-2017]

- (1) 1/8                      (2) 1/7  
(3) 3/8                      (4) 1/2



Also  $\frac{l_1}{l_2} = \sqrt{\frac{M_2}{M_1}}$

Where  $n_1$  and  $n_2$  are moles of gas-1 and gas-2,  
 $l_1$  and  $l_2$  are length travelled by gas-1 and gas-  
 2 respectively.

**Q20** If the rate of diffusion of hydrogen is 1 then find as the molecular weight of that gas which has rate of diffusion is equal to  $\frac{1}{4}$

- (1) 64            (2) 82            (3) 24            (4) 32

**Sol.** (4)

$$r \propto \frac{1}{\sqrt{M}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \quad r_1 = 1$$

$$4 = \sqrt{\frac{M_2}{2}}$$

$$16 = \frac{M_2}{2} \Rightarrow M_2 = 32$$

**Q21** If 50 ml of hydrogen diffuses in 20 minute from a small hole of tube then how much time will take by 40 ml of  $O_2$  to diffuse :

- (1) 12 min            (2) 64 min            (3) 8 min            (4) 32 min

**Sol.** (2)

$$\frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{50}{20} \times \frac{t_2}{40} = \sqrt{\frac{32}{2}}$$

$$\frac{5 \times t_2}{80} = 4$$

$$t_2 = \frac{80 \times 4}{5} = 64 \text{ mins}$$



**Q22** 2 gm of hydrogen diffuse from a container in 10 min. Has many gram of oxygen would diffuse through the same container in the same time under similar condition :

- (1) 5 gm      (2) 4 gm      (3) 6 gm      (4) 8 gm

**Sol.** (4)

$$\frac{w_1}{t_1} \times \frac{t_2}{w_2} = \sqrt{\frac{M_1}{M_2}}; \quad \frac{2}{10} \times \frac{10}{w_2} = \sqrt{\frac{2}{32}}$$

Therefore  $w_2 = 8$  gm

**Q23** The rate of diffusion of a gas is proportional to :

- (1)  $\sqrt{\frac{3P}{d}}$       (2)  $\frac{3P}{d}$       (3)  $\sqrt{\frac{3PV}{d}}$       (4)  $\frac{3PV}{M}$

**Sol.** (1)

$$r \propto \sqrt{\frac{3P}{d}}$$

**Q24** Calculate the molecular weight of a gas X which diffuses four times as fast as another gas Y, which in turn diffuses twice as fast as another gas Z. Molecular weight of the gas Z is 128.

**Sol.**

$$\begin{aligned} r_y &= 2r_z \\ \frac{r_y}{r_z} &= \frac{2r_z}{r_z} = \sqrt{\frac{128}{M_y}} \\ 4r_y &= \frac{128}{4} = 32 \\ r_x &= 4r_y \\ \frac{r_x}{r_y} &= \frac{4r_y}{r_y} = \sqrt{\frac{32}{M_x}} \\ M_x &= 2 \end{aligned}$$

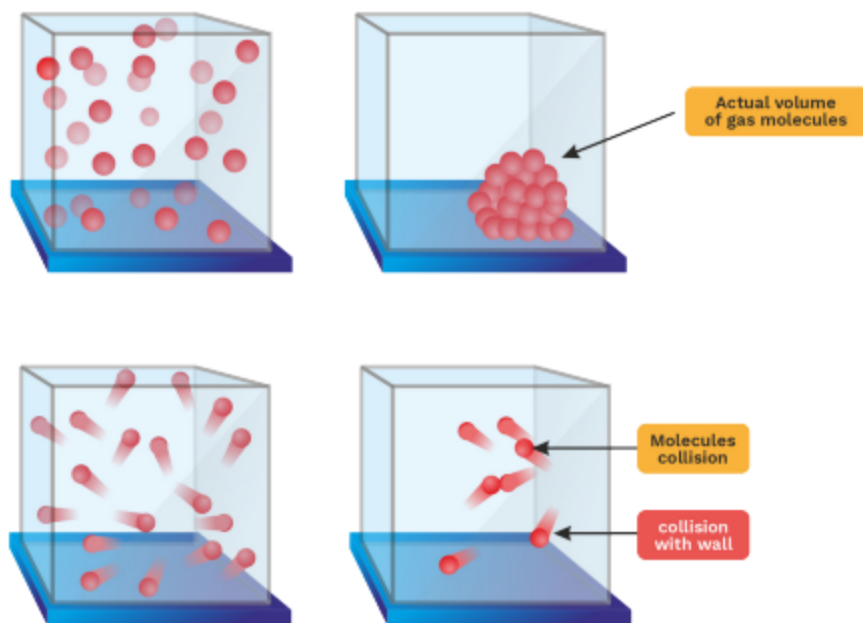


### Kinetic Theory of gases :

Gas laws were based on experimental data. Attempts were therefore been made to derive the theoretical aspect of laws. Maxwell succeeded in his attempt and gave the idea of kinetic theory of gases

#### A. Postulates

1. Gases has very tiny particles which are always in constant random motion because of the random movement of gaseous molecules gases exhibit the phenomenon of diffusion
2. Gravitational force doesn't affect the molecules of gases.
3. There exist no inter molecular attraction forces among the molecules of gases
4. The actual volume of a gas molecule in general is negligible as compared to the total volume of the gas.
5. Molecules of gas possess elastic nature in spite of infinite number of collisions and bombardment among themselves and against walls of the container, their average kinetic energy remains constant.



### Previous Year's Questions



If a gas expands at constant temperature, it indicates that

[AIPMT]

- (1) kinetic energy of molecules remains the same
- (2) number of the molecules of gas increases
- (3) kinetic energy of molecules decreases
- (4) pressure of the gas increases



6. The temperature of the gas is direct measure of its internal energy means kinetic energy of gas molecules depends only on absolute temperature
7. Gases have got very low density in comparison to liquids and solids
8. Gases can compressed or expanded by change in temperature and pressure conditions.
9. The properties of gases which can be conveniently measured are volume, pressure, temperature and masses

$$PV = nRT \Rightarrow PV = \frac{m}{M}RT$$

According to postulates kinetic gas equation

$$PV = \frac{1}{3}mnu^2$$

Where, P = pressure of the gas

V = volume of the gas

M = Mass of a molecule

u = Root means square velocity (RMS)

n = Number of molecules present in amount of gas

For 1 mole of gas  $n = N_A$  and  $m \times N_A = M$

$$\text{So } PV = \frac{1}{3}mu^2$$

Where M = molecular weight of gas

$$\Rightarrow \frac{1}{3}Mu^2 = RT \quad \Rightarrow \quad u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

### Rack your Brain



Kinetic energy of one mole of ideal gas at 300 K is?

### Previous Year's Questions



Average molar kinetic energy of CO and  $N_2$  at same temperature is

[AIPMT]

- (1)  $KE_1 = KE_2$
- (2)  $KE_1 > KE_2$
- (3)  $KE_1 < KE_2$
- (4) can't say anything. Both volumes are not given.

**Q25** The energy of an ideal gas is

- |                        |                          |
|------------------------|--------------------------|
| (1) Completely kinetic | (2) Completely potential |
| (3) KE + PE            | (4) All of the above     |

**Sol.** (1)  
Completely kinetic





**Q26** Gas at a pressure  $P_0$  is contained in a vessel. If the masses of all the molecules are halved and their speed doubled, the resulting pressure  $P$  will be equal to :

- (1)  $4P_0$                       (2)  $2P_0$                       (3)  $P_0$                       (4)  $\frac{P_0}{2}$

**Sol.** (2)

$$PV = \frac{1}{3}mnu^2$$

$$P' = 2P$$

• **Calculation of Kinetic Energy**

$$PV = \frac{1}{3}mnu^2$$

$$\therefore PV = RT$$

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

$$\therefore RT = \frac{2}{3} \times \frac{1}{3}Mu^2$$

$$\therefore \frac{3}{2}RT = \frac{1}{2}Mu^2$$

$$\therefore \text{K.E} = \frac{3}{2}RT \text{ for one mole}$$

• For  $n$  mole of gas

$$\text{Average K.E} = \frac{3}{2}nRT$$

Then for one molecule

$$\text{K.E} = \frac{3}{2} \frac{RT}{N} = \frac{3}{2}kT$$

$k$  is known as boltzman constant and i.e  $1.38$

$$\times 10^{-16} \frac{\text{erg}}{\text{K.molecule}}$$

For 1 mole of gas

$$\text{K.E} = \frac{3}{2}RT$$

**Previous Year's Questions**



The energy absorbed by each molecule ( $A_2$ ) of a substance is  $4.4 \times 10^{-19}$  J and bond energy per molecule is  $4.0 \times 10^{-19}$  J. The kinetic energy of the molecule per atom will be

[AIPMT]

- (1)  $2.2 \times 10^{-19}$  J  
 (2)  $2.0 \times 10^{-19}$  J  
 (3)  $4.2 \times 10^{-20}$  J  
 (4)  $2.0 \times 10^{-20}$  J



• **Average Speed :**

$$\therefore U_{\text{avg}} = \frac{U_1 + U_2 + \dots + U_n}{N}$$

$$\therefore U_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}}$$

$$\therefore U_{\text{rms}} : U_{\text{avg}} : U_{\text{mps}}$$

$$\therefore \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}}$$

$$\therefore 1.73 : 1.59 : 1.414$$

**Q27** Calculate the R.M.S and average velocity of hydrogen molecules at 0°C.

- (1)  $18.4 \times 10^4$  cm/s                      (2)  $18.4 \times 10^3$  cm/s  
 (3)  $16.9 \times 10^4$  cm/s                      (4)  $16.9 \times 10^3$  cm/s

**Sol.** (3)

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 10^7 \times 273}{2.016}}$$

$$u = 18.4 \times 10^4 \text{ cm/sec}$$

And

$$V = 0.921 \times u = 0.921 \times 18.4 \times 10^4 = 16.9 \times 10^4 \text{ cm/sec}$$

**Q28** The gas molecules have R.M.S velocity of its molecules as 1000 m/sec. What is its average velocity ?

- (1) 1012 m/sec (2) 921.58 m/sec                      (3) 546 m/sec                      (4) 960 m/sec

**Sol.** (2)

$$\text{R.M.S velocity} = \sqrt{\frac{3RT}{M}}$$

$$\Rightarrow \frac{V_{\text{rms}}}{V_{\text{avg}}} = \sqrt{\frac{3RT}{M} \times \frac{\pi M}{8RT}}$$

$$V_{\text{avg}} = \frac{V_{\text{rms}}}{\sqrt{\frac{3\pi}{8}}} = \frac{1000}{\sqrt{\frac{3\pi}{8}}} = \frac{1000}{3.06} \times \sqrt{8}$$

$$= 921.58 \text{ m/sec}$$

$$\text{Average velocity} = \sqrt{\frac{8RT}{\pi M}}$$



**Q29** Density ratio of  $O_2$  and  $H_2$  is 16 : 1 the ratio of its  $U_{rms}$  is:

- (1) 4 : 1      (2) 16 : 1      (3) 1 : 4      (4) 1 : 16

**Sol.**

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$
$$\frac{U_{O_2}}{U_{H_2}} = \sqrt{\frac{d_{H_2}}{d_{O_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$$

**Q30** The root mean square speed of the molecule of diatomic gas is  $u$ . When the temperature doubled, the molecules dissociated into atoms. The new RMS speed of the atom is :

- (1)  $\sqrt{2}u$       (2)  $u$       (3)  $2u$       (4)  $4u$

**Sol.** (3)

$$T_2 = 2T \Rightarrow \frac{M}{2}$$
$$U_1 = \sqrt{\frac{3RT}{M}}$$
$$U_2 = \sqrt{\frac{3R \times 2T \times 2}{M}}$$
$$\therefore V_2 = 2 \times V_1$$

**Q31** At what temperature will the average velocity of  $CH_4$  molecules has the same value as  $O_2$  has at 300 K ?

- (1) 1200 K      (2) 150 K      (3) 600 K      (4) 300 K

**Sol.** (3)

$$U_{avg} = \sqrt{\frac{8RT}{\pi M}}$$
$$\sqrt{\frac{T_1}{M_1}} = \sqrt{\frac{T_2}{M_2}}$$
$$\frac{300}{16} = \frac{T_2}{32}$$
$$\therefore T_2 = 600 \text{ K}$$

**Q32** Average speed at  $T_1$  K and the most probable speed at  $T_2$  K of  $\text{CO}_2$  gas is  $9 \times 10^4$  cm/sec. Calculate the value of  $T_1$  and  $T_2$  :

(1)  $T_1 = 1684$  K,  $T_2 = 2143$  K

(2)  $T_1 = 1500$  K,  $T_2 = 2100$  K

(3)  $T_1 = 782$  K,  $T_2 = 1050$  K

(4)  $T_1 = 1800$  K,  $T_2 = 2300$  K

**Sol.** (1)

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi M}}$$

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

$$\sqrt{\frac{8RT_1}{\pi M}} = \sqrt{\frac{2RT_2}{M}}; \quad \frac{T_1}{T_2} = \frac{\pi}{4}$$

For  $\text{CO}_2$ ,

$$\mu_{\text{mp}} = \sqrt{\frac{2RT}{M}} = 9 \times 10^4;$$

$$= \sqrt{\frac{2 \times 8.31 \times 10^7 \times T_2}{44}} = 9 \times 10^4$$

$$T_2 = 2143.37 \text{ K}; \quad T_1 = 1684 \text{ K}$$

### MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

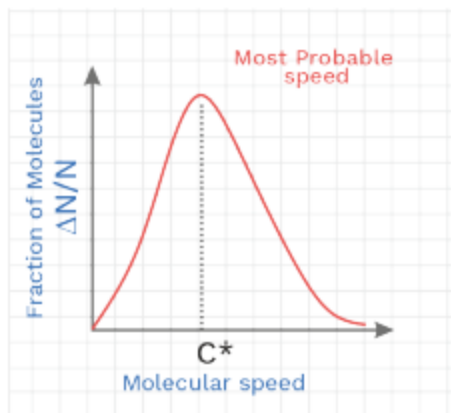
- The speeds of the individual molecules of gas do not remain constant. They keep on changing due to intermolecular collisions and due to collisions with the walls of the container. However, at a given temperature the distribution of molecular speeds does not change. The distribution of molecular speeds is given by Maxwell-Boltzmann distribution law.
- It may be noted that the fraction of molecules having the most probable speed remains same so long as temperature remains same.

### Concept Ladder



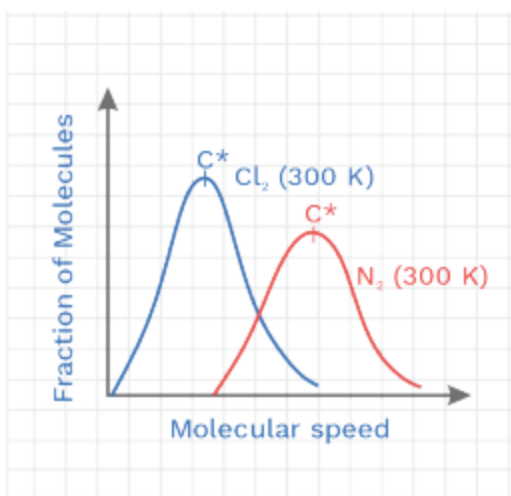
The fraction of molecules with very low or very high velocities (speeds) is very small.

The fraction of molecules possessing higher and higher speeds goes on increasing till it reaches the peak, and thereafter it starts decreasing.



The speed of the maximum number of molecules of the gas at a given temperature is known as the most probable speed of a gas, and it corresponds to the peak of the curve.

- At the same temperature, lighter gases shall move faster than heavier gases.



- **Effect of Temperature :  $[T_3 > T_2 > T_1]$**

It can be seen from these distribution curves that as the temperature increases.

- The entire curve shifts towards right.
- The most probable speeds increase on increasing temperature.
- The fraction of molecules having the most probable speed decreases.

### Previous Year's Questions



The temperature of a gas is raised from  $27^\circ\text{C}$  to  $927^\circ\text{C}$ . The root mean square speed of the gas

[AIPMT]

- (1) remains same
- (2) gets  $\sqrt{\frac{927}{27}}$  times
- (3) gets halved
- (4) gets doubled

### Concept Ladder



The assumptions of the kinetic theory are related to atoms and molecules which cannot be seen. Thus, the kinetic theory is said to give us a microscopic model of gases.

### Previous Year's Questions



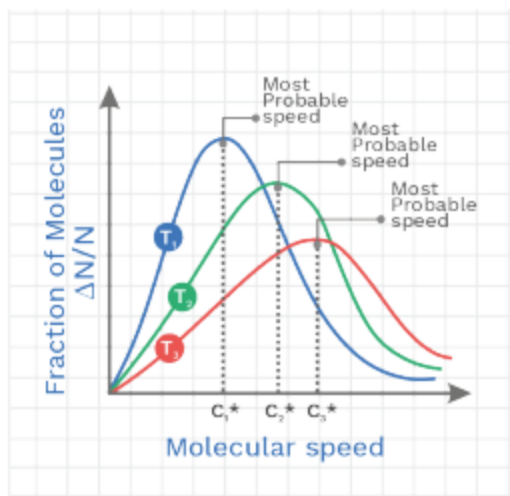
By what factor does the average velocity of a gaseous molecule increase when the temperature (in Kelvin) is doubled?

[AIPMT-2011]

- (1) 2.0
- (2) 2.8
- (3) 4.0
- (4) 1.4



- The fraction of molecules having higher speed increases.



### Rack your Brain



A gas will approach ideal behaviour at which condition?

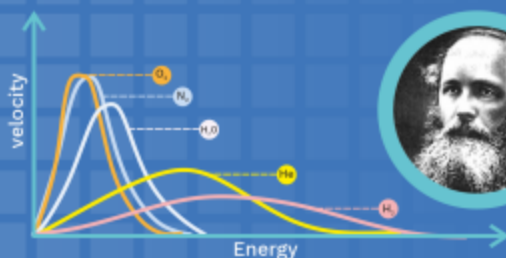
### Definitions

#### REAL GAS:

None of the gases present in universe strictly obey the equation  $PV = nRT$ , hence they are known as real or non ideal gases.

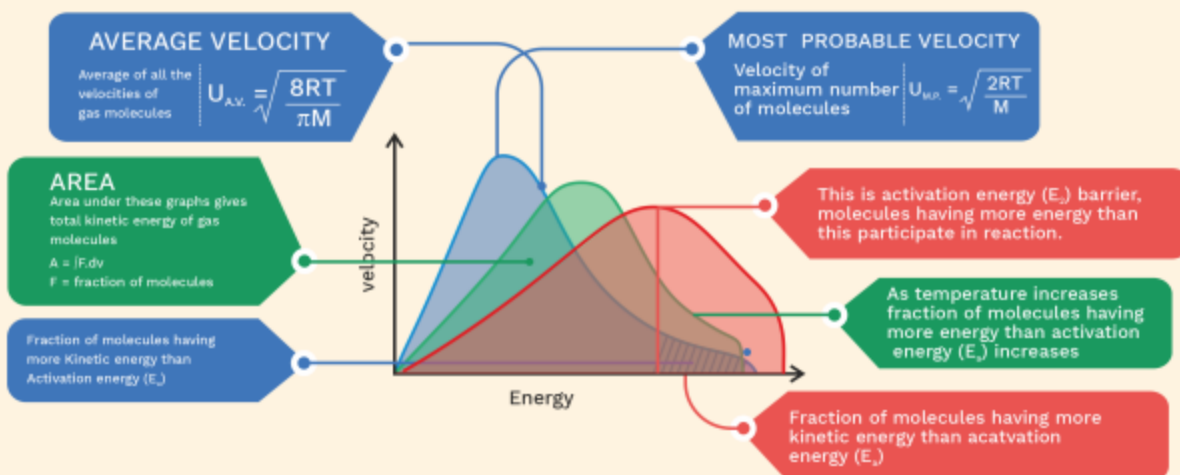
### Difference between Ideal Gas and Real Gas :

IDEAL GAS	REAL GAS
1. Obey all gas law	1. Do not obeys gas law
2. Obeys all postulates of K.T.G	2. Do not obeys postulates of K.T.G
3. There exist no intermolecular attraction forces among the molecules of ideal gases	3. There exist intermolecular attraction forces among the molecules of real gases which cannot be considered as negligible
4. The actual volume of an ideal gas in comparison to the volume occupied by the gas is very very less and hence the actual volume of the ideal gas can be considered as negligible or zero.	4. Actual volume of real gas cannot be considered as negligible or zero
5. Ideal gas exists at high temperature, low pressure condition	5. Real gas exists at low temperature and high pressure condition
6. $PV = nRT$ equation is applicable for ideal gases	6. It is not applicable to real gases as correction factor for pressure and volume are required.



## DISTRIBUTION OF MOLECULAR VELOCITIES

Maxwell Boltzmann stated, all molecules don't have similar velocity. Each molecule moves with different velocity.



## ROOT MEAN SQUARE VELOCITY

average velocity may be zero because velocity is vector,

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$

so we use root mean square velocity

**Q33** Which of the following gases will have the highest RMS velocity at 25°C?  
(1) O<sub>2</sub>                      (2) CO<sub>2</sub>                      (3) SO<sub>2</sub>                      (4) CO

**Sol.** (4)  
CO gas, because root mean square velocity =  $\left(\frac{3RT}{M_w}\right)^{1/2}$

**Deviation from the ideal gas behaviour :**

Deviation from ideal gas behaviour are observed particularly at high pressure and low temperature

The deviation can be displayed by compressibility factor (Z). It is the ratio of observed molar volume  $V_m$  to the ideal molar volume

$$\therefore Z = \frac{V_m}{V_{m,ideal}} = \frac{V_m}{\left(\frac{RT}{P}\right)} = \frac{V_m \times P}{RT}$$

**Note :**

1.  $Z = 1$  for ideal gas
2.  $Z > 1$ , means positive deviation usually at high pressure
3.  $Z < 1$ , means negative deviation usually at low pressure
4.  $Z > 1$ , for  $H_2$  and He at all pressure means always positive deviation.

**Causes of Deviation from ideal gas equation :****Vander waal's equation :****1. Volume correction :**

The volume inhabited by the gaseous molecules is negligible as compared to total volume of gas. So the observed volume is greater than ideal volume and correctly term  $nb$  has to be subtracted from observed volume in order to get ideal volume.

$$V_{obs} = V_{ideal} + nb \quad [V_{ideal} = V - nb]$$

Where  $n$  is number of moles of real gas and  $b$  is constant which depends on nature of real gas.

**Significance of constant 'b' :**

This constant  $b$  is called co-volume or non compressible volume. Its unit are lit/mol measured by effective size of gas molecules. Value of  $b$  is four times the actual volume of the molecules.

$$b = 4N.V.$$

**Concept Ladder**

At a very high pressure, the measured volume of  $H_2$  is more than the calculated volume. At low pressure, the measured and calculated volumes approach each other.

Deviation from ideal behaviour also becomes apparent when the PV vs P plot is drawn for several gases at 273 K.

**Previous Year's Questions**

The ratio among most probable velocity, mean square velocity is given by

**[AIPMT]**

- (1) 1 : 2 : 3
- (2)  $1 : \sqrt{2} : \sqrt{3}$
- (3)  $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$
- (4)  $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$





## 2. Pressure correction :

The force of attraction between the gaseous molecules are negligible at any condition, So the observed pressure is always less than ideal pressure.

Thus, a correction term  $\frac{an^2}{V^2}$  is added to

observed pressure.

$$P_{\text{ideal}} = P + \frac{an^2}{V^2}$$

### Significance of 'a' :

The value of 'a' gives idea of magnitude of attraction forces between molecules of gas. Its unit is  $\text{atm l}^2/\text{mol}^2$ .

The value of 'a' in general cases is maximum for  $\text{SO}_2$  than for  $\text{NH}_3$ . Larger the value of 'a', larger the intermolecular attraction among gas molecules and that gas will be easily liquefied

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

Where a and b are known as Vander waal's constant.

### Rack your Brain



What do you expect, "a" of a non polar gas to be more or of a polar gas to be more?

**Q34** Calculate the pressure exerted by 8.5 g of ammonia ( $\text{NH}_3$ ) contained in a 0.5 L vessel at 300 K. For ammonia,  $a = 4.0 \text{ atm L}^2 \text{ mol}^{-2}$ ,  $b = 0.036 \text{ L mol}^{-1}$ .

**Sol.** Number of moles of ammonia

$$n = \frac{8.5}{17} = 0.5 \text{ mol}$$

According to van der Waals equation

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

$$\begin{aligned} P &= \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} \\ &= \frac{0.5 \times 0.082 \times 300}{(0.5 - 0.5 \times 0.036)} - \frac{4(0.5)^2}{(0.5)^2} = 21.51 \text{ atm} \end{aligned}$$

### Determination of compressibility factor as per the vander waal's equation

Vander waal's equation :

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

V is the volume of n mole of gas

$V_m$  is the volume of 1 mole of gas

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \text{ At low pressure}$$

Volume is sufficiently large

$$\therefore \left(P + \frac{a}{V_m^2}\right)(V_m) = RT$$

$$P \cdot V_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$\therefore \left(\frac{V_m}{RT/P}\right) + \frac{a}{V_m RT} = 1$$

$$Z + \frac{a}{V_m RT} = 1$$

$$Z = 1 - \frac{a}{V_m RT} \text{ At high pressure}$$

At high value of P,  $V_m$  is small

$$\therefore P(V_m - b) = RT$$

$$\therefore PV_m - Pb = RT$$

$$\therefore \frac{PV_m}{RT} - \frac{Pb}{RT} = 1 \quad \therefore \frac{V_m}{(RT/P)} - \frac{Pb}{RT} = 1$$

$$\therefore Z = 1 + \frac{Pb}{RT}$$

(c) At high temperature and low pressure : Gas will behave like an ideal gas

$$\therefore PV = nRT$$

(d) Hydrogen and Helium : The value of 'a' is externally small for these gases as they are difficult to liquify.

### Previous Year's Questions



Given van der Waal's constant for  $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  are respectively 4.17, 0.244, 1.36 and 3.59 which one of the following gases is most easily liquefied.

[NEET-2018]

- (1)  $\text{NH}_3$                       (2)  $\text{H}_2$   
(3)  $\text{O}_2$                         (4)  $\text{CO}_2$

### Rack your Brain



Can you guess what will be the value of Z (compressibility factor) for a gas at its critical condition?

### Previous Year's Questions



A gas at 350 K and 15 bar has molar volume 20 percent smaller than for an ideal gas under the same conditions. The correct option about the gas and its compressibility factor (Z) is :

[NEET-2019]

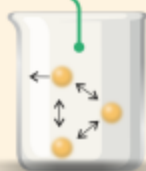
- (1)  $Z < 1$  and repulsive forces are dominant  
(2)  $Z > 1$  and attractive forces are dominant  
(3)  $Z > 1$  and repulsive forces are dominant  
(4)  $Z < 1$  and attractive forces are dominant

# WHAT MAKE GASES REAL ?

## DEVIATION FROM IDEAL GAS

### Pressure correction

Pressure is more on the walls of container by an ideal gas. In real gases, molecules have attraction between them, thus reducing the force applied on container.



### Volume correction

For ideal gas, V is equal to volume of container. However in real gases molecules occupy considerable Volume



$$P_{\text{real}} = P_{\text{ideal}} - \frac{an^2}{V^2}$$

$$(P + \frac{an^2}{V^2})(V-nb) = nRT$$

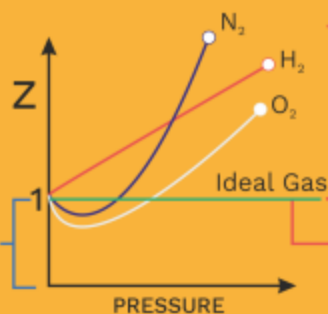
Van der Waal Equation

$$V_{\text{real}} = V_{\text{ideal}} + nb$$

## IS Z A REAL DETECTOR?

$$Z < 1$$

- ➔ Deviates from ideal gas behaviour
- ➔ Attractive forces dominate repulsive forces



$$Z < 1$$

- ➔ Deviates from ideal gas behaviour
- ➔ Attractive forces dominate repulsive forces

$$Z = 1 \Rightarrow \text{ideal gas}$$

AT LOW PRESSURE & HIGH TEMPERATURE real gas acts as ideal gas

### HELIUM & HYDROGEN

They are lighter gases. So force of attraction is less. Therefore, they have always  $Z > 1$ .

### VAN DER WAAL'S CONSTANT

- a - measure of average attraction of gas molecules
- b - proper volume of gas molecules. It is actually 4 times volume of single molecule.





**Q35** The behaviour of a real gas is usually depicted by plotting compressibility factor  $Z$  v/s  $P$  at a constant temperature. At high temperature and high pressure  $Z$  is usually more than one. This fact can be explained by vander waal's equation :

- (1) The constant  $a$  is negligible and not  $b$
- (2) The constant  $b$  is negligible and not  $a$
- (3) Both the constants  $a$  and  $b$  are negligible
- (4) Both the constants  $a$  and  $b$  are not negligible

**Sol.** (1)  
At high pressure

$$P + \frac{a}{V^2} = P$$

$$P(V-b) = RT$$

**Q36** At low pressure, Vander waal's equation is reduced to  $\left[ P + \frac{a}{V^2} \right] V = RT$ , the compressibility factor combination given as :

(1)  $1 - \frac{a}{RTV}$

(2)  $1 - \frac{RTV}{a}$

(3)  $1 + \frac{a}{RTV}$

(4)  $1 + \frac{RTV}{a}$

**Sol.** (1)  
The reduced van der Waal's equations is  $\left[ P + \frac{an^2}{V^2} \right] V = RT$

$$\Rightarrow PV + \frac{a}{V} = RT \text{ or } \frac{PV}{RT} + \frac{a}{RTV} = 1 ;$$

$$\Rightarrow \frac{PV}{RT} = \left( 1 - \frac{a}{RTV} \right) = z$$

#### Deviation from ideal gas behaviour :

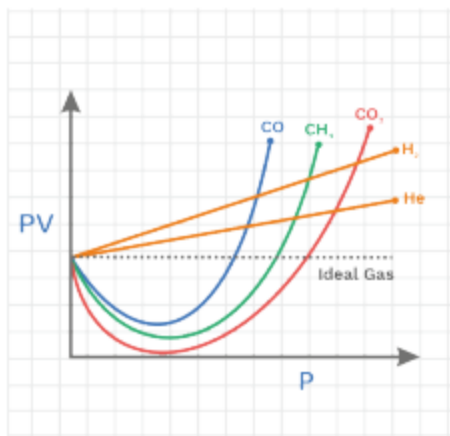
1. According to Boyle's law:  $PV = \text{constant}$  at constant temperature. Hence at constant temperature  $PV$  v/s  $P$  is a straight line parallel to  $x$ -axis

#### Rack your Brain

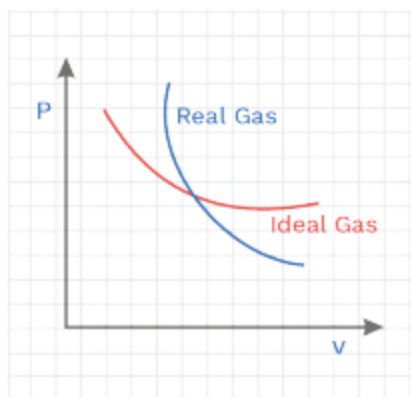


Can you predict the conditions at which a real gas will behave like an ideal gas ?

2. According to graph for  $H_2$  and He PV increases continuously with increase of pressure.
3. While of gas  $CO$ ,  $CH_4$  etc. PV first decreases with increase of pressure and reaches a minimum value and then increase continuously with increase of pressure



4. At intermediate pressure  $CO_2$  shows much large negative deviation than  $H_2$  and  $N_2$ .



- i. At high pressure, the observed volume is more than calculate volume. Means volume of real gas is more than ideal gas so, gas show real gas behavior
- ii. At intermediate pressure, the observed volume and calculated volume approach each other.

### Concept Ladder



Gases like  $H_2$ , He at 273 K are seen to be less compressible than the ideal gas at all pressure i.e.,  $Z > 1$ .

### Rack your Brain



Liquification of gases takes places at certain temperatures. Can liquification takes places at high temperature than the fix temperature?

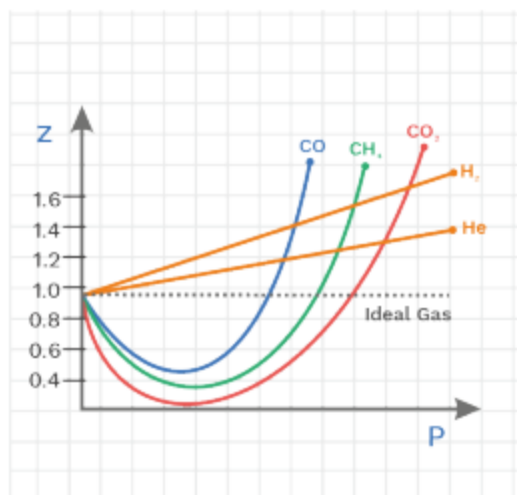
### Concept Ladder



On the other hand  $Z-P$  plots of gases like  $NH_3$ ,  $CO$ ,  $CH_4$  etc., are similar to those of  $H_2$ , He at 273 K, if the temperature is sufficiently high..



- iii. At low pressure the observed volume is less than calculated volume so, volume of ideal gas is more than real gas means ideal gas behavior.



- I. If  $Z = 1$ ,  $PV = RT$  – Ideal gas
- II. When ( $Z < 1$ ) (eg. For  $\text{CH}_4$  and  $\text{CO}_2$ )  
Negative deviation means gas is more compressible in compare to ideal behaviour.
- III. ( $Z > 1$ ) Positive deviation occurs generally at high pressure
- IV. ( $\text{H}_2$  and He) gas is less compressible than ideal behaviour due to strong repulsive force among molecule and size of  $\text{H}_2$  and He molecule is very small, so greater the value of  $Z$  from unity, greater the deviation from ideal behaviour

#### Liquification of Gases :

The phenomenon of converting a gas into liquid is known as liquification. The liquification of gas is achieved by controlling  $P$  and  $T$

##### 1. Increasing Pressure :

An increase in pressure increases attraction among molecules.

#### Rack your Brain



Compressibility factor for an ideal gas is?

#### Concept Ladder



Greater the value of 'a' easier the liquification of gas ; greater the value of 'b' greater the molecular size.

#### Previous Year's Questions



A gas such as carbon monoxide would be most likely to obey the ideal gas law at : **[NEET-2015]**

- (1) Low temperature and high pressure
- (2) High temperatures and high pressures
- (3) Low temperatures and low pressure
- (4) High temperatures and low pressure



## 2. Decreasing Temperature :

A decrease in temperature results in decrease in kinetic energy of molecules. The temperature of gas must be lower than its critical temperature  $T_c$ .

### Critical Temperature ( $T_c$ )

It is defined as the characteristic temperature for a given gas below which a continuous increases in pressure will bring liquification of gas and above which no liquefaction takes place.

$$T_c = \frac{8a}{27Rb}$$

Eg.  $T_c$  for  $\text{CO}_2$  is  $30.98^\circ\text{C}$

### Critical pressure ( $P_c$ )

It is defined as the minimum pressure applied on 1 mole of gas placed at critical temperature to just liquify the gas

$$P_c = \frac{a}{27b^2}$$

### Critical volume ( $V_c$ )

The volume occupied by 1 mole of gas placed at critical conditions

$$\text{i.e. } \frac{P}{T} = \frac{P_c}{T_c} \text{ and } V_c = 3b$$

### General Points :

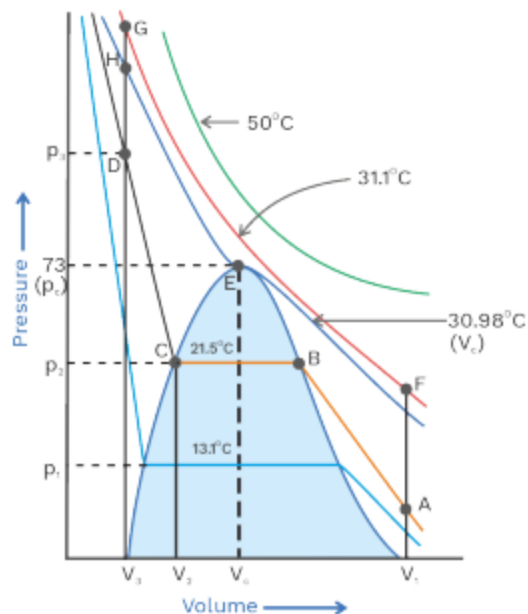
1. The numerical values of critical constant are :

$$T_c = \frac{8a}{27Rb}$$

$$P_c = \frac{a}{27b^2} \text{ [a and b are Vander waal's constant]}$$

$$V_c = 3b$$

2. For the gas having its temperature much lower than its critical temperature high pressure is sufficient to liquify it.



### Concept Ladder



The parameters  $T_c$ ,  $P_c$  and  $V_c$  for a gas are collectively called **critical constants**.

### Concept Ladder



Critical point refers to the state of a substance at critical temperature and critical pressure.



### Liquid State - General Properties

- They have definite volume but not definite shape.
- As compared to gases, density of liquids is higher but is lower than that of solids.
- As compared to solids, their compressibility is greater but is less than that of gases as small voids are present between liquid molecules.
- The diffusion rate is slower in comparison to gases than that of gases but more than that of solids due to small voids and slow molecular motion by liquids.
- The distance of separation between the molecules of a liquid is in the range of  $10^{-7}$  to  $10^{-9}$  m.
- Liquids diffuse slowly as the molecules of liquids undergo large number of collisions with the neighbouring molecules.
- A liquid resembles a gas near critical temperature of the gas and a solid near the melting point of solid.

### Vapour Pressure

- Vapour pressure is the pressure, at a particular temperature, exerted by vapours over liquid surface when vapours are in equilibrium with liquid. Vapour pressure increases with increase in temperature. The variation of vapour pressure of liquid with temperature is given as

$$\log P = \frac{-A}{T} + 1$$

A = Constant

P = Vapour Pressure of liquid

T = Temperature

- The plot of  $\log P$  vs  $\frac{1}{T}$  will be a straight line.

At boiling point,

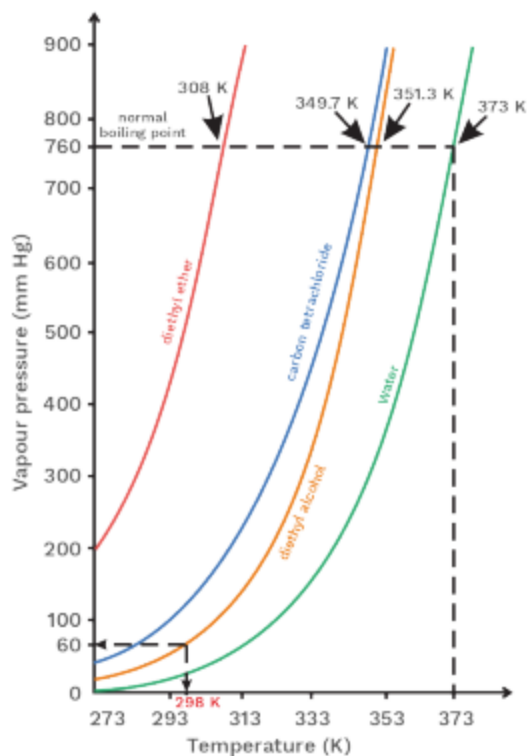
vapour pressure = atmospheric pressure

The vapour pressure of  $H_2O$  at 373 K is 76 cm of Hg.

### Concept Ladder



Boiling is a special case of evaporation. It is the rapid conversion of a liquid into vapours by means of formation of bubbles. During boiling, evaporation is not restricted to the surface only but takes place throughout the bulk of the liquid.





- At critical temperature, the meniscus between liquid and vapour disappears.
- Vapour pressure  $\propto$  extent or strength of H-bonding.  
For example, HF > H<sub>2</sub>O > NH<sub>3</sub>
- Heat of vaporization  $\propto$  extent or strength of H-bonding, for example, HF > H<sub>2</sub>O > NH<sub>3</sub>
- Amount of heat required to change a gram of a liquid into vapours at the boiling point of liquid is known as heat or enthalpy or latent heat of vaporization.

#### Trouton's law

$$\frac{\Delta H_{\text{vap}}}{T_b} = 21 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$\Delta H_{\text{vap}}$  = Heat of vaporization

$T_b$  = Boiling point of a liquid

#### Clausius-Clapeyron equation

It explains the effect of temperature on vapour pressure of a liquid and also explains the effect of pressure on the boiling point of a liquid.

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303 R} \cdot \frac{(T_2 - T_1)}{(T_1 \cdot T_2)}$$

#### Difference Between Evaporation and Boiling Processes

- During evaporation, cooling occurs as the average kinetic energy of the liquid decreases since molecules with higher kinetic energy leave the surface to form vapours.
- Boiling occurs only at a specific temperature while evaporation can take place at any temperature.
- Boiling occurs below the surface while evaporation occurs only at surface.

#### Surface Tension

- Surface tension is the force at right angles to the surface of a liquid along one cm or one metre (unit) length of the surface.

#### Concept Ladder



The amount of enthalpy required to convert a liquid into gas at a constant temperature is known as the enthalpy of vapourisation.

#### Definitions

Molar enthalpy of vapourisation ( $\Delta_{\text{vap}} H$ ) is defined as the amount of enthalpy required to convert 1 mol of a liquid to gas at the boiling point of the liquid.

#### Previous Year's Questions



The beans are cooked earlier in pressure cooker because :

[AIPMT-2011]

- (1) boiling point increases with increasing pressure
- (2) boiling point decreases with increasing pressure
- (3) extra pressure of pressure cooker softens the beans
- (4) internal energy is not lost while cooking in pressure cooker.



- Its units are: Newton metre<sup>-1</sup> or [N m<sup>-1</sup>], dyne cm<sup>-1</sup>.
- Due to surface tension the surface area of the liquid decreases to minimum, for example, falling drops are spherical. Sphere is the minimum surface area for a given volume.
- Due to surface tension a liquid rises in the capillary tube, water moves upwards in soil and some insects are able to walk on the surface of water.
- Surface tension  $\propto \frac{1}{\text{Temperature}}$
- At critical temperature, surface tension is zero.
- The effect of temperature is given by **Eotvos equation.**  

$$\gamma = K(T_c - T)(d/M)^{2/3}$$

Where,

K = Constant

d = Density

M = Molar mass

#### Measurement of surface tension

To measure surface tension, a stalagmometer is used. It is based on the principle that surface tension is directly proportional to the amount or weight of the spherical drop falling from the vertically kept capillary tube.

$$\gamma \propto M \quad \text{so} \quad \frac{r_1}{r_2} = \frac{M_1}{M_2}$$

#### Surface Energy

Surface energy is work done in ergs required to increase the surface area by 1 square centimetre. Its units are erg/cm<sup>2</sup> or Joule/m<sup>2</sup>.

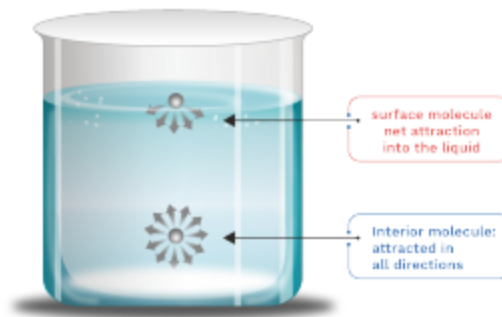
#### Viscosity

The property due to which it resists the flow is known as viscosity. It increases with increase of temperature.

#### Concept Ladder



The net force of attraction acting on such a molecule is almost zero. A molecule at the surface of the liquid has no upper molecules to participate in attraction.



#### Concept Ladder



Surface energy  
 = work per sq cm  
 = (force × length) per sq. cm  

$$= \frac{\text{dynes} \times \text{cm}}{\text{cm}^2} = \text{dynes cm}^{-1}$$



### Viscosity coefficient ( $\eta$ )

Viscosity coefficient is the force of friction needed to maintain a velocity difference of  $1 \text{ cm sec}^{-1}$  between any two parallel layers of  $1 \text{ cm}^2$  area and which are  $1 \text{ cm}$  apart.

$$\eta = \frac{f \cdot x}{A \cdot v} = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{sec}^{-1}} = \text{dyne cm}^{-2} \text{ sec}$$

$$= 1 \text{ poise}$$

Where,

$f$  = Force

$a$  = Area

$v$  = Velocity difference

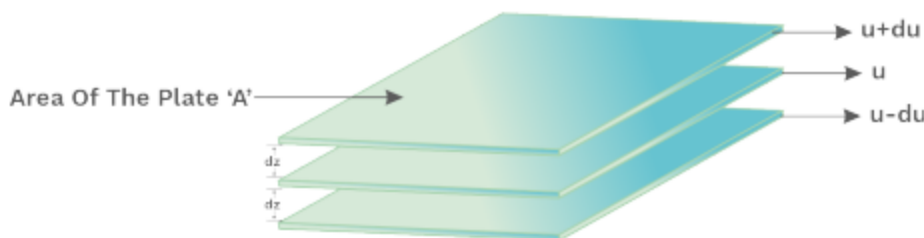
$x$  = Distance between two layers

$1 \text{ poise} = 1 \text{ g cm}^{-1} \text{ sec}^{-1}$

Since  $\text{dyne} = \text{g} \times \text{cm} \times \text{sec}^{-2}$

$1 \text{ poise} = \frac{1}{10} \text{ Newton metre}^2 \text{ sec}^{-1}$

or  $\text{pas}$  or  $\text{kg m}^{-1} \text{ s}^{-1}$



### Effect of temperature on viscosity

It can be shown by Arrhenius equation as follows :

$$\eta = A e^{E_a/RT}$$

Where,

$T$  = Temperature

$R$  = Universal gas constant

$E_a$  = Activation energy

### Measurement of viscosity

- When the same volume of two liquids say X and Y are flowing from the same height and through the same capillary then



$$\frac{\eta_x}{\eta_y} = \frac{d_x t_x}{d_y t_y}$$

Where,

$d_x$  = Density of liquid x

$d_y$  = Density of liquid y

$t_x$  = Time for flow of liquid x

$t_y$  = Time for flow of liquid y.

- Ostwald viscometer is used to measure viscosity.

### Fluidity

It is the reciprocal of viscosity coefficient of a liquid denoted by  $\phi$ .

$$\phi = \frac{1}{\eta}$$

**Q37** Calculate the pressure exerted by one mole of  $\text{CO}_2$  gas at 273 K if the van der Waals constant  $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-1}$ . Assume that the volume occupied by  $\text{CO}_2$  molecules is negligible.

**Sol.** The van der Waals equation for one mole of a gas is

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

It is given that the volume occupied by  $\text{CO}_2$  molecules is negligible. Hence, the equation of state becomes

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

$$\text{or } P = \frac{RT}{V} - \frac{a}{V^2}$$

Assuming  $V_m = 22.414 \text{ dm}^3 \text{ mol}^{-1}$ , we get

$$\begin{aligned} P &= \frac{(8.314)(273)}{22.414} - \frac{3.592}{22.414} \\ &= 101.264 - 0.160 \\ &= 101.104 \text{ kPa} \end{aligned}$$



**Q38** A truck carrying oxygen cylinders is filled with oxygen at  $-23^{\circ}\text{C}$  and at a pressure of 3 atmosphere in Srinagar, Kashmir. Determine the internal pressure when the truck drives through Madras, Tamil nadu. Where the temperature is  $30^{\circ}\text{C}$ :

**Sol.**  $P_1 = 3 \text{ atm}, P_2 = ?$   
 $T_1 = -23 + 273 = 250 \text{ K}$   
 $T_2 = 273 + 30 = 303 \text{ K}$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
$$\frac{3}{250} = \frac{P_2}{303}$$
$$P_2 = \frac{3 \times 303}{250} = 3.64 \text{ atm}$$

**Q39** Calculate the weight of  $\text{CH}_4$  in a 9 litre cylinder at 16 atm and  $27^{\circ}\text{C}$  ( $R = 0.08 \text{ lit. atm/K}$ ).

**Sol.** Given  $P = 16 \text{ atm}, V = 9 \text{ litre}$   
 $T = 300 \text{ K}, m_{\text{CH}_4} = 16, R = 0.08 \text{ litre atm/k.}$

$$PV = w/m \times R \times T$$
$$16 \times 9 = \frac{w}{16} \times 0.08 \times 300$$
$$w = 96 \text{ gm}$$

**Q40** 5gm of  $\text{XeF}_4$  gas was introduced into a vessel of 6 litre capacity at  $80^{\circ}\text{C}$ . What is the pressure of the gas in atmosphere :

**Sol.** Given  $V = 6 \text{ litre},$   
 $T = 353 \text{ K}, R = 0.082, W = 5\text{gm. } m = 207.3$

$$PV = \frac{W}{m} \times R \times T$$
$$P \times 6 = \frac{5}{207.3} \times 0.082 \times (273 + 80)$$
$$P = \frac{5 \times 0.082 \times 353}{6 \times 207.3} = 0.11 \text{ atm} = 0.11 \text{ atm.}$$

**Q41** A mixture of gases at 760 mm pressure contains 65% nitrogen, 15% oxygen and 20% Carbondioxide by volume. What is the partial pressure of each in mm :

**Sol.**

$$P'_{N_2} = 760 \times \frac{65}{100} = 494 \text{ mm}$$
$$P'_{O_2} = 760 \times \frac{15}{100} = 114 \text{ mm}$$
$$P'_{CO_2} = 760 \times \frac{20}{100} = 152 \text{ mm}$$

**Q42** The total pressure of a sample of methane collected over water is 735 torr at 29°C. The aqueous tension at 29°C is 30 torr. What is the pressure exerted by dry methane :

**Sol.**

$$P_{\text{total}} = P_{\text{dry methane}} + P_{\text{water}}$$
$$735 = P_{\text{dry methane}} + 30$$

$\therefore P_{\text{dry methane}} = 735 - 30 = 705 \text{ torr.}$

**Q43** The volumes of ozone and chlorine diffusing during the same time are 35 ml and 29 ml respectively. If the molecular weight of chlorine is 71. Calculate molecular mass of ozone.

**Sol.**

$$\frac{r(O_3)}{r(Cl_2)} = \sqrt{\frac{M(Cl_2)}{M(O_3)}}$$

Rate of diffusion in same time is proportional to volume diffused so

$$\frac{V(O_3)}{V(Cl_2)} = \sqrt{\frac{M(Cl_2)}{M(O_3)}}$$

$$\frac{(35)^2}{(29)^2} = \frac{71}{M(O_3)}$$

$$M(O_3) = 48.74$$



## Summary



### Gas Law's

#### (1) Boyle's Law

$$P_1V_1 = P_2V_2$$

#### (2) Charle's Law

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

#### (3) Gay lussac's Law

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

#### (4) Avogadro's Law

$V \propto$  moles  $\propto$  number of molecules (P & T const.)

### Graham's Diffusion Law

It is applicable for non reacting gases

$$r \propto \frac{1}{\sqrt{d}}$$

### Dalton's Law of Partial Pressure

$$P_{\text{mixture}} = P_1 + P_2 + P_3 \dots\dots (T \& V \text{ const.})$$

### Kinetic gas Equation

$$PV = \frac{1}{3}mNu_{\text{rms}}^2$$

Where,

$N_0$  = Avogadro number

$u$  = Root Mean Square velocity

### Average KE ( $KE_{\text{av}}$ )

$$KE_{\text{av}} = \frac{3}{2}nRT \quad (\text{m moles})$$

$$KE_{\text{av}} = \frac{3}{2}KT \quad (1 \text{ molecules})$$



$$V_{\text{rms}} = \sqrt{\frac{V_1^2 + V_2^2 + \dots + V_n^2}{N}}$$

$$V_{\text{av}} = \frac{V_1 + V_2 + V_3 + \dots + V_n}{N}$$

$$V_{\text{rms}} = \sqrt{\frac{3RT}{Mw}}$$

$$V_{\text{av}} = \sqrt{\frac{8RT}{\pi Mw}}$$

$$V_{\text{mp}} = \sqrt{\frac{2RT}{Mw}}$$

$$V_{\text{rms}} = \sqrt{\frac{3PV}{Mw}}$$

$$V_{\text{av}} = \sqrt{\frac{8PV}{\pi Mw}}$$

$$V_{\text{mp}} = \sqrt{\frac{2PV}{Mw}}$$

$$V_{\text{rms}} = \sqrt{\frac{3P}{d}}$$

$$V_{\text{av}} = \sqrt{\frac{8P}{\pi d}}$$

$$V_{\text{mp}} = \sqrt{\frac{2P}{d}}$$

### Compressibility factor (Z)

$$Z = \frac{(V_m)_{\text{obs}}}{V_i} = \frac{P(V_m)_{\text{obs}}}{RT}$$

If  $z = 1$ , the gas show ideal gas behaviour

If  $z > 1$ , the gas show positive deviation

If  $z < 1$ , the gas show negative deviation

### Vander waal's Equation

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

$$P_i = P_R + \frac{an^2}{V^2} \Rightarrow P_i > P_R$$