

GASEOUS STATE

GASEOUS STATE

1. GAS

Gas is defined as that state of matter which has a definite volume but no definite shape. They take up the shape of the vessel in which they are kept.

2. CHARACTERISTICS OF GASES

- 2.1 Gases or the gaseous mixtures are quite homogeneous in composition.
- 2.2 Gases possess high compressibility and infinite expandability.
- 2.3 Gases have the property of diffusion.
- 2.4 Gases exert pressure on the walls of the containing vessel.
- 2.5 Density of matter is very low in gaseous state.
- 2.6 Gases can be converted into liquid state by cooling under high pressure.

3. GAS LAWS

All the gases undergo similar changes when their temperature & pressure are changed, this behaviour of gases is governed by some laws, known as gas laws.

4. BOYLE'S LAW

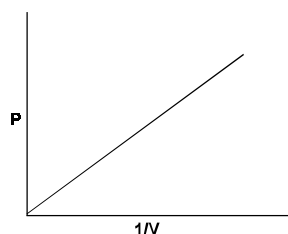
- 4.1 The volume of a given mass of a gas is inversely proportional to its pressure at constant temperature

$$\text{i.e. } V \propto \frac{1}{P}$$

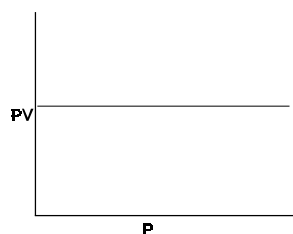
or $PV = \text{constant}$ (at constant temperature)

or $P_1V_1 = P_2V_2$ (at constant T)

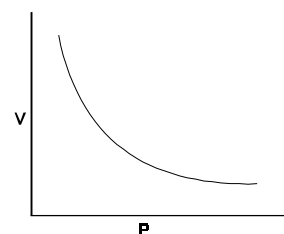
- 4.2 (a) Plot of P vs $1/V$ at constant T is a straight line passing through the origin.
(b) Plot of PV v/s P is a straight line Parallel to x - axis.
(c) Plot of V v/s P is a hyperbola
- 4.3 Density of a gas is directly proportional to its Pressure. At altitudes, as Pressure is low, density of air is less. That is why mountaineers carry oxygen cylinders.
- 4.4 Air is dense at the sea level because it is compressed by the mass of air above it. However the density and Pressure decreases with altitude. The atmospheric Pressure at mount-everest is only 0.5 atm.
- 4.5 Graphical representation of Boyle's law
The plots of P v/s V at constant temp. are known as isotherms. These are shown below.



(a)



(b)



(c)

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5. CHARLES LAW

- 5.1** The volume of a given mass of a gas is directly proportional to the temperature in kelvin scale (absolute scale) at constant pressure.

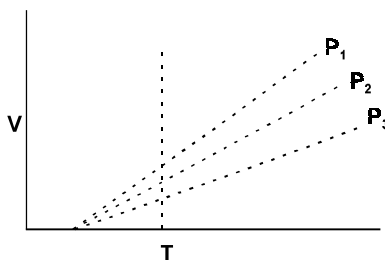
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{at constant pressure})$$

- 5.2** At constant pressure the volume of a given mass of a gas increases or decreases by $1/273$ of its volume at 0°C for every rise or fall of one degree in temperature.

$$V_t = V_0 + \frac{V_0}{273} \times t \quad (\text{at constant pressure})$$

$$= V_0 \left(1 + \frac{t}{273}\right) = V_0 \left(\frac{273+t}{273}\right)$$

- 5.3** The plot of volume and temperature at constant pressure are known as isobars. A straight line is obtained.



6. IDEAL GAS EQUATION

Based on gas laws, Boyle's and Charles law, the following mathematical expression is derived,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad \frac{PV}{T} = k \quad (\text{constant})$$

7. ABSOLUTE ZERO

Absolute zero is the theoretically possible temperature at which the volume of the gas becomes zero. It is equal to 0 K or -273°C . At this temperature, the total KE of the molecules is zero.

$$\text{KE} = \frac{3}{2} RT$$

$$t^\circ\text{C} = (273 + t^\circ\text{C}) \text{ K}$$

8. STP AND NTP

Standard temperature and pressure (STP) or normal temperature and pressure (NTP)

$$P = 1 \text{ atm.} \quad T = 0^\circ\text{C} \quad \text{or} \quad 273 \text{ K}$$

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9. GAS CONSTANT (R)

9.1 Nature of gas constant R

$$R = \frac{P \times V}{nT} = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Degree K}} = \frac{(\text{Force} / \text{Area}) \times (\text{Volume})}{\text{Moles} \times \text{Degrees}}$$
$$= \frac{\text{Force}}{(\text{length})^2} \times \frac{(\text{length})^3}{\text{Moles} \times \text{Degrees}} = \frac{\text{Force} \times \text{length}}{\text{Moles} \times \text{Degrees}}$$

= Work per degree per mol

9.2 Units of gas constant (R)

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

(Hence $P = 1 \text{ atm}$, $V = 22.4 \text{ L}$, $T = 273 \text{ K}$, $1 \text{ L} = 1 \text{ dm}^3$)

$$= 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

when P is expressed in dynes per square centimeter ($P = 76 \times 981 \times 13.6 \text{ dynes cm}^{-2}$);
 $V = 221400 \text{ cc}$ and $T = 273 \text{ K}$

$$\text{then } R = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$$
$$= 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

R can also be expressed in calories since work and heat produced are related by Joules's relationship,
 $W = J H$

where J = Mechanical equivalent of heat ($4.184 \times 10^7 \text{ ergs per calorie}$)

$$\text{Thus } R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

In S.I. units pressure is expressed in pascal (Pa)

$$1 \text{ atm. pressure} = 0.76 \text{ m} \times 13.6 \times 10^3 \text{ kg m}^{-3} \times 9.81 \text{ ms}^{-2}$$
$$= 101325 \text{ Nm}^{-2} = 101325 \text{ Pa}$$

$$\text{Thus, the gas constant } R = \frac{101325 \times 22400 \times 10^{-6}}{273}$$

$$= 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} \text{ (SI units)}$$

$$= 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \text{ MPa cm}^3 \text{ K}^{-1} \text{ mol}^{-1} \text{ (SI units)}$$

The value of R can also be given in electron volts per degree per mol.

1eV is the energy acquired by electron in falling through a potential difference of one volt.

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ volts coulomb (Joule)}$$

$$\therefore R = \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1}}{1.602 \times 10^{-19} \text{ eV}}$$

$$= 5.189 \times 10^{19} \text{ eV K mol}^{-1}$$

Gas constant, R is work done Per degree Per mole. Values of Gas constant (R)

Units of P	Units of V	Units of R
Atmosphere	Litres	$0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$
Atmosphere	cm^3	$82.1 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
Dynes cm^{-2}	cm^3	$8.31 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$ $= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$

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10. BOLTZMANN CONSTANT (K)

Gas constant per molecule is known as Boltzmann constant (K)

$$K = \frac{R}{N} = 1.36 \times 10^{-10} \quad \text{ergs/ K/ molecule or } 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$$

11. AVOGADRO'S LAW

According to this law "Equal volumes of all gases, measured at the same temperature and pressure, contain equal number of molecule", i.e.

$V \propto N$ (at constant temperature and pressure)

1 gram mole (mol. mass in grams) of all gases at NTP (STP) occupies 22.4 litres or $(22400 \times 10^{-6} \text{ m}^3)$. This volume is referred as molar volume.

1 mole of any substance contains equal number of molecules which is known as Avogadro's number and denoted by N and equal to 6.023×10^{23} . With the help of this number of the mass in gram of one molecule can be calculated, i.e. the mass of 1 molecule of nitrogen (mol. mass 28).

$$= \frac{28 \text{ g mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} = 4.649 \times 10^{-23} \text{ g.}$$

12. DALTON'S LAW OF PARTIAL PRESSURE

12.1 If two or more gases which do not react chemically are enclosed in a vessel, the total Pressure exerted by the gaseous mixture is equal to the sum of all the Partial Pressures that each would exert when present alone in the same vessel at the same temperature.

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

12.2 Dalton's Law fails in those gases which react chemically.

12.3 Partial pressure = Mole fraction \times Total pressure

12.4 Aqueous Tension is the pressure exerted by the water vapours at a given temperature. It is temperature dependent. It can be calculated with the help of Dalton's law.

$$\text{Aqueous tension} = P_{\text{Total}} - P_{\text{dry gas}}$$

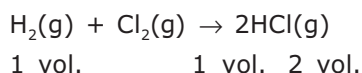
13. AMAGAT LAW OF PARTIAL VOLUME

It states that the total volume of mixture of gases which do not react at constant temperature and pressure is equal to the sum of the individual partial volume of the constituents.

$$V = v_1 + v_2 + v_3 + \dots + v_n = \sum v_i$$

14. GAY-LUSSAC'S LAW

According to this law, "when gases react, the volume of these gases, and the volumes of the products formed (if gaseous) are in simple whole number ratio to each other". e.g.



The ratio is 1 : 1 : 2 (a simple ratio).

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15. GRAHAM'S LAW OF DIFFUSION

15.1 Graham's law states that under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square roots of their molecular masses or their vapour densities or directly proportional to its pressure.

$$15.2 \quad r_{\text{diffusion}} \propto \sqrt{\frac{1}{M}} \quad \text{or} \quad \sqrt{\frac{1}{d}}$$

$$15.3 \quad r_{\text{diffusion}} \propto p$$

$$15.4 \quad \frac{v_1}{t_1} \cdot \frac{t_2}{v_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

$$15.5 \quad \frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

15.6 Diffusion : Intermixing of gases irrespective of force of gravity is known as diffusion. It refers to the flow of molecules from a region of high concentration to a region of low concentration.

15.7 Effusion : The passage of gases through a small aperture under pressure is known as effusion. Graham's law of diffusion is also applicable to effusion.

16. BAROMETRIC DISTRIBUTION LAW

We know that for gaseous systems gravitation force is negligible but it is not true for the gases of high molecular mass such as polymer. In this case the pressure will be different in different vertical positions in a container. It is observed that pressure of the gas decreases with increase in its height from the ground. This relation may be given as :

$$p = p^0 e^{-Mgh/RT}$$

where p^0 and p are the pressures of the gas at the ground level and at a height 'h' from the ground respectively, M is molecular mass of the gas, g is acceleration due to gravity, R is gas constant and T is temperature in kelvin.

Since number of moles of gas, 'n' and density of the gas are directly proportional to pressure hence the above equation may be expressed as :

$$d = d^0 e^{-Mgh/RT}$$

$$\text{and} \quad n = n^0 e^{-Mgh/RT}$$

The above equations may be expressed as :

$$\begin{aligned} \log \frac{p}{p^0} &= \log \frac{d}{d^0} = \log \frac{n}{n^0} \\ &= - \frac{1}{2.303} \times \frac{Mgh}{RT} \end{aligned}$$

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SOLVED EXAMPLES

Q.1 A perfect gas of a given mass is heated first in a small vessel and then in a large vessel, such that their volume remains unchanged. The P – T curves are :

- (A) Parabolic with same curvature (B) Linear with different slope
(C) Linear with same slope (D) Parabolic with different curvature

Ans. (B)

$$\begin{aligned} \therefore \quad & PV = nRT \\ \text{First} \quad & P_1V_1 = nRT_1 \\ \text{and} \quad & P_2V_2 = nRT_2 \\ \therefore \quad & \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \end{aligned}$$

Thus P – T curves are linear but with different slopes.

Q.2 If the inter molecular forces vanish away, the volume occupied by the molecules contained in 4.5 kg. water at STP will be :

- (A) 5.6 m³ (B) 6.5 m³ (C) 11.2 litre (D) 7.5 m².

Ans. (A)

Mole of water evaporated = $\frac{4.5 \times 10^3}{18}$; Now calculate volume of vapours assuming 1 mole occupies 22.4 litre.

Q.3 At a constant pressure, what should be the percentage increase in the temperature in kelvin for a 10% increase in volume :

- (A) 10% (B) 18% (C) 30% (D) 5%.

Ans. (A)

Use $V \propto T$ then

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

If $V_2 = \left[V_1 + \frac{10V_1}{100} \right]$. Find T_2 and calculate percent change.

Q.4 Which of the following gases will have the same rate of effusion under identical conditions ?

- (i) CO (ii) CO₂ (iii) N₂O (iv) C₂H₄ (v) C₃H₈.
(A) CO, CO₂, C₂H₄ (B) CO₂, C₂H₄, N₂O
(C) C₃H₈, N₂O, CO₂ (D) CO, N₂O, C₂H₄, C₃H₈.

Ans. (C)

Q.5 A gas can be liquified by :

- (A) Cooling (B) Compressing (C) Both of these (D) None of these.

Ans. (C)

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Q.6 According to Charles's law at constant pressure, 100 ml of a given mass of a gas with 10°C rise in temperature will become :

- (A) 100.0366 (B) 99.9634 (C) 103.66 (D) 100.366.

Ans. (C)

Q.7 The density of a gas X is 1.5 times that of Y. The molecular weight of X is M. The molecular weight of Y is :

- (A) $\frac{M}{1.5}$ (B) 1.5 M (C) $\frac{M}{3}$ (D) 3 M.

Ans. (A)

Q.8 The ratio of masses of oxygen and nitrogen in a gaseous mixture is 1 : 4. The ratio of number of molecules is :

- (A) 1 : 4 (B) 7 : 32 (C) 1 : 8 (D) 3 : 16.

Ans. (B)

Let the mass of mixture = Wg

$$\text{Amount of O}_2 \text{ in mixture} = \frac{W}{5 \times 32} \text{ mol}$$

$$\text{Amount of N}_2 \text{ in mixture} = \frac{4W}{5 \times 28} \text{ mol}$$

$$\text{So ratio of number of molecules} = \frac{W}{5 \times 32} : \frac{4W}{5 \times 28}$$

$$= \frac{1}{32} : \frac{1}{7} = 7 : 32.$$

Q.9 A gas is contained in a vessel. If the pressure is halved and the absolute temperature is doubled; the volume of the gas :

- (A) Will be doubled (B) Will be 1/4th of original volume
(C) Will remain same (D) Will increase four times.

Ans. (D)

$$\text{In initial state } V_1 = \frac{nRT}{P}$$

$$\text{In final state } V_2 = \frac{nR \cdot 2T}{1/2 P} = \frac{4nRT}{P}$$

$$\text{Hence } V_1 : V_2 = \frac{nRT}{P} : \frac{4nRT}{P} = 1 : 4.$$

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Q.10 One mole of N_2O_4 (g) at 300K is kept in a closed vessel under 1 atm. It is heated to 600K when 20% by mass of N_2O_4 (g) decomposes to NO_2 . The resultant pressure is :

- (A) 1.2 atm (B) 2.4 atm (C) 2.0 atm (D) 1.0 atm.

Ans. (B)



$$\text{At } t = 0, \quad 100 \text{ g} = \frac{100}{92} \text{ mol}$$

$$\text{At } t_{eq}, \quad 80 \text{ g} = \frac{80}{92} \text{ mol}$$

$$20 \text{ g} \equiv \frac{20}{46} \text{ mol}$$

$$\text{Now} \quad P_0V = n_0 RT$$

$$(1 \text{ atm.}) V = \left[\frac{100}{92} \text{ mol.} \right] R (300 \text{ K}) \quad \dots\dots\dots (1)$$

$$P_1V = n_1 RT$$

$$P_1V = \left[\left(\frac{80}{92} + \frac{20}{46} \right) \text{ mol} \right] (R) (600K)$$

$$P_1V = \left[\frac{120}{92} \text{ mol} \right] (R) (600K) \quad \dots\dots\dots(2)$$

By dividing equation 2 by 1 :

$$\frac{P_1}{1 \text{ atm.}} = \frac{120 \times 600}{100 \times 300} = 2.4.$$

$$P_1 = 2.4 \text{ atm.}$$

Q.11 One mole of N_2 gas at 0.8 atm. takes 38 seconds to diffuse through a pin hole ; where as one mole of an unknown compound of Xenon with fluorine at 1.6 atm. takes 57 seconds to diffuse through the same hole. The molecular formula of the compound is :

- (A) XeF_4 (B) XeF_6 (C) Xe_2F_2 (D) Xe_2F_6 .

Ans. (B)

The rate of diffusion depends on the following :

$$r \propto P \text{ and } r \propto \sqrt{\frac{1}{M}}$$

Taking these factors together, we get

$$\frac{r_2}{r_1} = \frac{P_2}{P_1} \left[\frac{M_1}{M_2} \right]^{1/2}, \quad \left[\text{Since } r \propto \frac{1}{t} \right]$$

$$\text{Hence} \quad \frac{t_1}{t_2} = \frac{P_2}{P_1} \left[\frac{M_1}{M_2} \right]^{1/2}$$

$$M_2 = \left[\frac{P_2 \cdot t_2}{P_1 \cdot t_1} \right]^2 M_1$$

If subscript 1 = N₂ and 2 = unknown gas, then :

$$M_2 = \left[\frac{1.6}{0.8} \times \frac{57}{38} \right]^2 (28 \text{ g mol}^{-1})$$

$$M_2 = 252 \text{ g mol}^{-1}$$

Let the molecular formula of the unknown compound be XeF_n. Then M_{Xe} + nM_F = 252 g mol⁻¹ that is

$$[131 + n(19)] \text{ g mol}^{-1} = 252 \text{ g mol}^{-1}$$

$$n = \frac{252 - 131}{19}$$

$$= 6.3 \cong 6$$

Hence, the molecular formula of the gas is XeF₆.

Q.12 The pressure exerted by 12 gm. of an ideal gas at temperature *t*°C in a vessel of volume *V* is 1 atm. When the temperature is increased by 10°C at the same volume, the pressure increases by 10%. If molecular weight of the gas is 120. The temperature *t* and volume *V* are :

(A) *t* = - 273°C, *V* = 0.082 L

(B) *t* = - 173°C, *V* = 0.82 L

(C) *t* = 0°C; *V* = 22.4 L

(D) *t* = 27°C, *V* = 22.4 L.

Ans. (B)

From the expression *PV* = *nRT*, we can get

$$\frac{P_1}{P_2} = \frac{T_1}{T_2} \quad (V \text{ and } n \text{ are constant})$$

By placing the values :

$$\frac{1 \text{ atm.}}{1.1 \text{ atm.}} = \frac{(273 + t^\circ\text{C}) \text{ K}}{(273 + t^\circ\text{C} + 10) \text{ K}}$$

or $283 + t^\circ\text{C} = (1.1)(273 + t^\circ\text{C})$

or $t^\circ\text{C} = \frac{283 - 1.1 \times 273}{0.1} = - 173.$

or $t = - 173^\circ\text{C}$

For the given system - $n = 12\text{g}/120 \text{ g. mol}^{-1} = 0.1 \text{ mol.}$

$$T = (273 - 173) \text{ K} = 100 \text{ K}$$

Hence $V = \frac{nRT}{P}$

$$= \frac{(0.1 \text{ mol})(0.082 \text{ L.atm.K}^{-1} \text{ mol}^{-1})(100 \text{ K})}{1 \text{ atm.}}$$

$$V = 0.82 \text{ L.}$$

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Q.13 An empty evacuated glass vessel weighs 50.0g, 148.0g when filled with a liquid of density 0.98 g ml⁻¹ and 50.5 g when filled with an ideal gas at 760mm Hg. at 300K. The molar mass of gas is :

- (A) 123 g. mol⁻¹ (B) 321 g. mol⁻¹ (C) 132 g. mol⁻¹ (D) 113 g. mol⁻¹.

Ans. (A)

$$\text{Mass of liquid filled } (m_1) = (148.0 - 50.0) = 98.0 \text{ g}$$

$$\text{Volume of glass vessel } V = \frac{m_1}{d} = \frac{98.0\text{g}}{0.98\text{gm.L}^{-1}} = 100 \text{ mL}$$

i.e., $V = 100 \text{ mL} = 0.1 \text{ dm}^3.$

Mass of gas filled in the vessel,

$$m = (50.5 - 50.0) \text{ g} = 0.5 \text{ g}$$

If M is the molar mass of gas, then we have

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

$$M = \frac{mRT}{PV}$$

$$M = \frac{(0.5\text{g})(8.314\text{Jk}^{-1}\text{mol}^{-1})(300\text{K})}{(101.325\text{kPa})(0.1\text{dm}^3)}$$

$$= 123 \text{ g mol}^{-1}.$$

Q.14 The vapour density of a mixture containing NO₂ and N₂O₄ is 38.3 at 27°C. The mole of NO₂ in 100 g mixture is :

- (A) 0.437 (B) 0.347 (C) 0.734 (D) Can not be predicted.

Ans. (A)

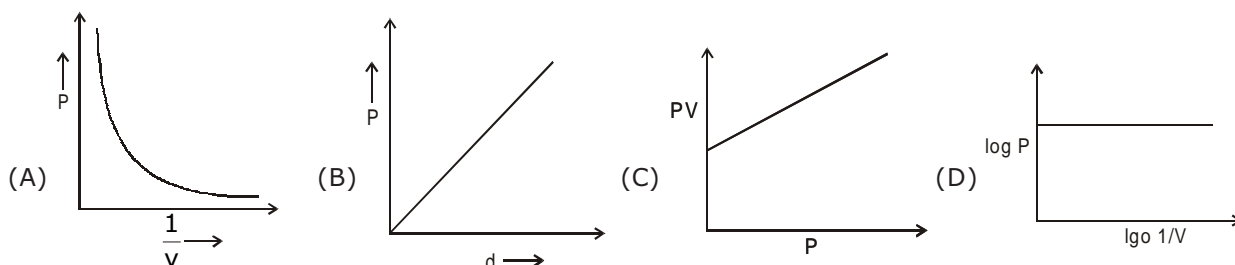
$$\text{Mol wt. of mixture} = 38.3 \times 2 = 76.6$$

$$\frac{x}{46} + \frac{100-x}{92} = \frac{100}{76.6}$$

$$x = 20.10 \text{ g}$$

$$\text{Mole of NO}_2 = \frac{20.10}{46} = 0.437.$$

Ex.15 Which of the following represents the Boyle's law -



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Sol. (B)

Since, density

$$d = \frac{1}{v} \text{ and}$$

according to Boyle's law $P \propto \frac{1}{v}$ (at constant T) so, the graph of the P vs. $\frac{1}{v}$ or d will be a straight line passing through origin.

Ex.16 Densities of two gases are in the ratio 1 : 2 and their temperatures are in the ratio 2 : 1, then the ratio of their respective pressure is -

(A) 1 : 1

(B) 1 : 2

(C) 2 : 1

(D) 4 : 1

Sol. (A)

$$\text{Given; } \frac{d_1}{d_2} = \frac{1}{2}, \frac{T_1}{T_2} = \frac{2}{1}, \frac{p_1}{p_2} = p$$

$$\text{Sin } \theta, \quad \frac{p_1 v_1}{p_2 v_2} = \frac{RT_1}{RT_2} \quad \Rightarrow \quad \frac{p_1}{p_2} \cdot \frac{v_1}{v_2} = \frac{T_1}{T_2}$$

$$\Rightarrow \frac{p_1}{p_2} = \frac{T_1 v_2}{T_2 v_1}$$

$$\Rightarrow \frac{p_1}{p_2} = \frac{T_1}{T_2} \cdot \frac{d_1}{d_2}$$

$$\left[\begin{array}{l} \frac{1}{v_1} = d_1 \\ \frac{1}{v_2} = d_2 \end{array} \right]$$

$$\Rightarrow \frac{p_1}{p_2} = \frac{2}{1} \cdot \frac{1}{2}$$

$$\text{Here } \frac{p_1}{p_2} = \frac{1}{1}$$

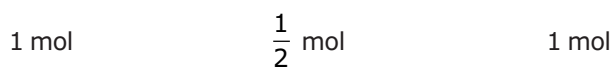
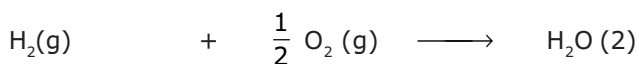
Ex.17 A mixture of hydrogen & oxygen (45 ml.) is sparked to form liquid water. The compound not in excess reacts completely and 15 ml is left over (all measurements are at the same temp. and pressure). The composition by volume in the original mixture of $H_2 : O_2$ is -

(A) 4 : 5

(B) 7 : 2

(C) either 4 : 5 or 7 : 2 (D) 2 : 1

Sol. (C)



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It means that hydrogen & oxygen reacts in the ratio of 2 : 1 by volume.

Total volume of mixture of H_2 & O_2 = 45 ml.

The component left (H_2 or O_2) after
reaction is = 15 ml.

Total volume of H_2 & O_2 reacted = 30 ml

Hence, H_2 O_2
20 ml 10 ml Total (30 ml.)

So, initially H_2 & O_2 will be in the ratio -

$$\begin{array}{r} H_2 \quad \quad O_2 \\ 20 \text{ ml} + 15 \text{ ml} \quad \quad 10 \text{ ml} \quad \Rightarrow \quad 7 : 2 \\ = 35 \end{array}$$

$$\begin{array}{r} \text{or} \quad 20 \text{ ml} \quad 10 \text{ ml} + 15 \text{ ml} \quad \Rightarrow \quad 4 : 5 \\ = 25 \text{ ml.} \end{array}$$

Ex.18 To which of the following gaseous mixtures is Dalton's law not applicable -

(A) Ne + He + SO_2 (B) NH_3 + HCl + HBr (C) O_2 + N_2 + CO_2 (D) N_2 + H_2 + O_2

Sol. (B)

NH_3 and HCl & HBr is a reacting gas mixture to produce NH_4Cl & NH_4Br so Dalton's law is not applicable.

Ex.19 A cylinder of 5 litre capacity, filled with air at NTP is connected with another evacuated cylinder of 30 litres of capacity. The resultant air pressure in both the cylinders will be -

(A) 10.8 cm of Hg (B) 14.9 cm of Hg (C) 21.8 cm of Hg (D) 38.8 cm of Hg

Sol. (A)

Given that

P_1 = 76 cm. of Hg. (initial pressure at NTP)

P_2 = ? , v_1 = 5 liter, v_2 = 30 + 5 = 35 liter

According to Boyle's law -

$$\begin{array}{l} P_1 V_1 = P_2 V_2 \\ 76 \times 5 = P_2 \times 35 \end{array}$$

$$P_2 = \frac{76 \times 5}{35} = 10.8 \text{ cm . g Hg.}$$

Ex.20 Volume of the air that will be expelled from a vessel of 300 cm^3 when it is heated from 27°C to 37°C at the same pressure will be -

(A) 310 cm^3 (B) 290 cm^3 (C) 10 cm^3 (D) 37 cm^3

Sol. (C)

According to Charles' law -

$$\frac{v_1}{v_2} = \frac{T_1}{T_2}$$

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

$$v_2 = \frac{T_2}{T_1} \cdot v_1$$

$$T_2 = 273 + 37 = 320^\circ \text{ K}$$

GASEOUS STATE

$$v_2 = \frac{310}{300} \times 300$$

$$v_1 = 300 \text{ cm}^3$$

$$v_2 = 310 \text{ cm}^3.$$

$$v_2 = ?$$

$$\text{Amount of gas expelled } \Delta V = v_2 - v_1 = 310 - 300 = 10 \text{ cm}^3$$

- Ex.21** A sample of O_2 gas is collected over water at 23°C at a barometric pressure of 751 mm Hg. (vapour pressure of water at 23°C is 21 mm Hg.). The partial pressure of O_2 gas in the sample collected is-
- (A) 21 mm Hg (B) 751 mm Hg (C) 0.96 atm (D) 1.02 atm

Sol. (C)

$$\begin{aligned} \text{Pressure of } \text{O}_2 \text{ (dry)} &= P(\text{total}) - P(\text{water vapour}). \\ &= 751 - 21 = 730 \text{ mm Hg.} \end{aligned}$$

$$= \frac{730}{760} = 0.96 \text{ atm.}$$

- Q.22** A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C . Due to a sudden fire in the building the temperature starts rising. At what temperature will the cylinder explode ?

(A) 100°C (B) 99.5°C (C) 150°C (D) 120°C

Sol. (B)

Since the gas is confined in a cylinder, its volume will remain constant.

Initial conditions

Final conditions

$$P_1 = 12 \text{ atm}$$

$$P_2 = 14.9 \text{ atm}$$

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

$$T_2 = ?$$

Applying pressure-temperature law,

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

$$\text{So } T_2 = \frac{P_2 \times T_1}{P_1} d$$

$$= \frac{14.9 \times 300}{12}$$

$$= 372.5 \text{ K}$$

$$\text{Temperature in } ^\circ\text{C} = (372.5 - 273) = 99.5^\circ\text{C}$$

- Q.23** 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular mass of the gas ?

(A) 45 (B) 52 (C) 41.33 (D) 60

Sol. (C)

For hydrogen,

$$w = 0.184 \text{ g}; \quad T = 25 + 273 = 290 \text{ K}; \quad M = 2$$

$$\text{We know that } PV = \frac{w}{M} RT$$

$$= \frac{0.184}{2} \times R \times 290 \quad \dots\dots(i)$$

For unknown gas,

$$w = 3.7 \text{ g}; \quad T = 25 + 273 = 298 \text{ K}; \quad M = ?$$

$$PV = \frac{3.7}{M} \times R \times 298 \quad \dots\dots(ii)$$

Equating both the equations,

$$\frac{3.7}{M} \times R \times 298 = \frac{0.184}{2} \times R \times 290$$

$$\text{or} \quad M = \frac{3.7 \times 298 \times 2}{0.184 \times 290} = 41.33$$

Q.24 A car tyre has a volume of 10 litre when inflated. The tyre is inflated to a pressure of 3 atm at 17°C with air. Due to driving the temperature of the tyre increases to 47°C (a) What would be the pressure at this temperature ? (b) How many litres of air measured at 47°C and pressure of 1 atm should be let out to restore the tyre to 3 atm at 47°C ?

(A) 3.1 atm , 0.31 litre (B) 3.31 atm , 3.1 litre (C) 0.31 atm , 0.31 litre (D) 3.1 atm , 3.1 litre

Sol. (B)

At constant volume,

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

$$\text{or} \quad \frac{3}{290} = \frac{P_2}{320}$$

$$\text{or} \quad P_2 = \frac{320 \times 3}{290} = 3.31 \text{ atm}$$

(b) Pressure to be decreased in tyre
= 3.31 - 3.0 = 0.31 atm

Let the volume of the gas to be taken out at 1 atmospheric pressure be V. As the temperature remains constant i.e., 47°C, Boyle's law can be applied to determine V.

$$1 \times V = 0.31 \times 10$$

$$\text{or} \quad v = 3.1 \text{ litre}$$

Q.25 The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of V litre is one atmosphere. When the temperature is increased by 10°C at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V (Molecular mass of the gas = 120).

(A) 100 k , 0.82 Litre (B) 200 k , 4 Litre (C) 273 k , 2 Litre (D) 173 , 3 Litre

Sol. (A)

As the volume is constant, pressure law can be applied, i.e.,

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

or
$$\frac{1}{1.1} = \frac{t + 273}{t + 283}$$

or $t = -173^{\circ}\text{C} = 100 \text{ K}$

Now, applying gas equation,

$$PV = nRT$$

or
$$V = \frac{n}{P} RT = \frac{12 \times 0.082 \times 100}{120 \times 1} = 0.82 \text{ litre.}$$

Q.26 If 200 mL of N_2 at 25°C and a pressure of 250 mm are mixed with 350 mL of O_2 at 25°C and a pressure of 300 mm so that the volume of resulting mixture is 300 mL, what would be the final pressure of the mixture at 25°C ?

- (A) 616.6 mm (B) 506.6 mm (C) 516.6 mm (D) 576.6 mm

Sol. (C)

In the case of nitrogen, volume increases, its pressure must decrease. Let the new pressure be P_{N_2} .

$$P_{\text{N}_2} = \frac{250 \times 200}{300} = 166.6 \text{ mm} \quad (\text{Applying Boyle's law})$$

In the case of oxygen, volume decreases, its pressure must increase. Let the new pressure be P_{O_2} .

$$P_{\text{O}_2} = \frac{300 \times 350}{300} = 350 \text{ mm} \quad (\text{Applying Boyle's law})$$

$$\text{Total pressure} = P_{\text{N}_2} + P_{\text{O}_2} = (166.6 + 350) = 516.6 \text{ mm}$$

Q.27 20 dm³ of SO_2 diffuse through a porous partition in 60 s. What volume of O_2 will diffuse under similar conditions in 30 s ?

- (A) 24 . 13 dm³ (B) 13 . 2 dm³ (C) 15 . 73 dm³ (D) 14 . 1 dm³

Sol. (D)

$$\text{Rate of diffusion of } \text{SO}_2 = \frac{20}{60} \text{ dm}^3 \text{ s}^{-1}$$

$$\text{Rate of diffusion of } \text{O}_2 = \frac{V}{30} \text{ dm}^3 \text{ s}^{-1}$$

According to Graham's law of diffusion,

$$\frac{(V / 30)}{(20 / 60)} = \sqrt{\frac{M_{\text{SO}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{64}{32}}$$

$$V = 14.1 \text{ dm}^3$$

GASEOUS STATE

UNSOLVED PROBLEMS

- Q.1** At constant temperature, the product of pressure and volume of a given amount of a gas is constant. This is :
(A) Gay-Lussac law (B) Charles' Law (C) Boyle's law (D) Pressure law
- Q.2** A curve drawn at constant temperature is called an isotherm. This shows the relationship between :
(A) P and $\frac{1}{V}$ (B) PV and V (C) V and $\frac{1}{P}$ (D) P and V
- Q.3** Charles' law is represented mathematically as :
(A) $V_t = KV_0t$ (B) $v_t = \frac{KV_0}{t}$ (C) $V_t = V_0\left(1 + \frac{273}{t}\right)$ (D) $V_t = V_0\left(1 + \frac{t}{273}\right)$
- Q.4** Correct gas equation is :
(A) $\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$ (B) $\frac{V_1T_2}{P_1} = \frac{V_2T_1}{P_2}$ (C) $\frac{P_1T_1}{V_1} = \frac{P_2T_2}{V_2}$ (D) $\frac{V_1V_2}{T_1T_2} = P_1P_2$
- Q.5** In general gas equation, $PV = nRT$, V is the volume of :
(A) n mole of a gas (B) any amount of a gas
(C) one mole of a gas (D) one gram of a gas
- Q.6** In the equation of state of an ideal gas $PV = nRT$, the value of universal gas constant would depend only on :
(A) The nature of the gas (B) The units of measurement
(C) The pressure of the gas (D) The temperature of the gas
- Q.7** The value of gas constant per degree per mol is approximately :
(A) 1 cal (B) 2 cal (C) 3 cal (D) 4 cal
- Q.8** Which one of the following is not the value of R ?
(A) 1.99 cal $K^{-1} mol^{-1}$ (B) 0.0821 lit-atm $K^{-1} mol^{-1}$
(C) 9.8 Kcal $K^{-1} mol^{-1}$ (D) 8.3 J $K^{-1} mol^{-1}$
- Q.9** One litre of a gas collected at NTP will occupy at 2 atmospheric pressure and 27°C :
(A) $\frac{300}{2 \times 273}$ litre (B) $\frac{2 \times 300}{273}$ litre (C) $\frac{273}{2 \times 300}$ litre (D) $\frac{2 \times 273}{300}$ litre
- Q.10** 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping the volume constant; its pressure would become :
(A) $\frac{1}{2}$ atm (B) $\frac{1}{273}$ atm (C) 2 atm (D) 273 atm

GASEOUS STATE

- Q.11** 300 mL of a gas at 27°C is cooled to -3°C at constant pressure; the final volume is :
(A) 540 mL (B) 135 mL (C) 270 mL (D) 350 mL
- Q.12** 273 mL of a gas at STP was taken to 27°C and 600 mm pressure. The final volume of the gas would be :
(A) 273 mL (B) 300 mL (C) 380 mL (D) 586 mL
- Q.13** The density of the gas is equal to :
(A) nP (B) MP/RT (C) P/RT (D) M/V
[P = Pressure; V = Volume; T = Temperature; R = Gas constant; n = number of mole; M = molecular mass]
- Q.14** The volume of a gas at 0°C is 273 mL. Its volume at 1°C and same pressure will be :
(A) $\frac{274}{273}$ mL (B) 274 mL (C) 272 mL (D) $\frac{273}{274}$ mL
- Q.15** Compressed oxygen is sold at a pressure at 100 atmospheres in a cylinder of 49 litre. The number of moles of oxygen in the cylinder is :
(A) 400 (B) 100 (C) 300 (D) 200
- Q.16** If the pressure and absolute temperature of 2 litre of carbon dioxide are doubled, the volume of carbon dioxide would become :
(A) 7 litre (B) 5 litre (C) 4 litre (D) 2 litre
- Q.17** One gram mole of a gas at NTP occupies 22.4 litre as volume. This fact was derived from :
(A) Dalton's theory (B) Avogadro's hypothesis
(C) Berzelius hypothesis (D) Law. of gaseous volumes
- Q.18** The V.D. of a gas is 11.2. The volume occupied by 11.2 g of this gas at NTP is :
(A) 1 litre (B) 2.24 litre (C) 11.2 litre (D) 22.4 litre
- Q.19** Five gram each of the following gases at 87°C and 750 mm pressure are taken. Which of them will have the least volume ?
(A) HF (B) HCl (C) HBr (D) HI
- Q.20** If molecular mass of O₂ and SO₂ are 32 and 64 respectively. If one litre of O₂ at 15°C and 750 mm pressure contains N molecules, the number of molecules in two litre of SO₂ under the same conditions of temperature and pressure will be :
(A) 2N (B) N (C) N/2 (D) 4N
- Q.21** The mass of 6.02×10^{23} molecules of CO is :
(A) 28 g (B) 14 g (C) 7.0 g (D) 56 g
- Q.22** 10 g of hydrofluoric acid occupy 5.6 litres of volume at NTP. The empirical formula of the gas is HF. The molecular formula of the gas will be (at. mass of fluorine = 19) :
(A) H₄F₄ (B) HF (C) H₃F₃ (D) H₂F₂

GASEOUS STATE

- Q.23** A fire extinguisher contains 4.4 kg of CO₂. The volume of CO₂ delivered by this fire extinguisher at room temperature is :
(A) 24.5 litre (B) 100 × 24.5 litre (C) 10 × 24.5 litre (D) 1000 × 24.5 litre
- Q.24** The number of moles of H₂ in 0.224 litre of hydrogen gas at STP is :
(A) 1 (B) 0.1 (C) 0.01 (D) 0.001
- Q.25** Mass of 112 mL of oxygen at NTP on liquefaction will be :
(A) 0.32 g (B) 0.96 g (C) 0.64 g (D) 0.16 g
- Q.26** Select the correct statement :
In the gas equation PV = nRT
(A) n is the number of molecules of a gas (B) n moles of the gas have volume V
(C) V denotes volume of one mole
(D) P is the pressure of the gas when only one mole of gas is present
- Q.27** The density of a gas at 27°C and 1 atm is d. Pressure remaining constant, at which of the following temperatures will its density become 0.75 d ?
(A) 20°C (B) 30°C (C) 400 K (D) 300 K
- Q.28** Absolute zero is the temperature where all gases are expected to have :
(A) Different volumes (B) Same volume (C) Zero volume (D) None of these
- Q.29** If a gas is heated at constant pressure, its density :
(A) will decrease (B) will increase
(C) may increase or decrease (D) will remain unchanged
- Q.30** Density of neon will be highest at :
(A) STP (B) 0°C, 2 atm (C) 273°C, 1 atm (D) 273°C, 2 atm
- Q.31** When the universal gas constant (R) is divided by Avogadro's number (N), their ratio is called :
(A) Planck's constant (B) Rydberg's constant
(C) Boltzmann's constant (D) Van der Waals' constant
- Q.32** 16 g of oxygen and 3 g of hydrogen are mixed and kept at 760 mm pressure at 0°C. The total volume occupied by the mixture will be nearly :
(A) 22.4 litre (B) 33.6 litre (C) 44800 mL (D) 4480 mL
- Q.33** Which of the following expressions does not represent Boyle's law ?
(A) PV = constant (B) $V \propto \frac{1}{P}$ (C) $V_1 T_2 = V_2 T_1$ (D) $P_1 V_1 = P_2 V_2$
- Q.34** Boyle's law may be represented as :
(A) $\left(\frac{dP}{dV}\right)_T = K/V$ (B) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V}$ (C) $\left(\frac{dP}{dV}\right) = -\frac{K}{V^2}$ (D) $\left(\frac{dP}{dV}\right)_T = \frac{K}{V^2}$

GASEOUS STATE

Q.35 According to Charles' law :

- (A) $V \propto \frac{1}{T}$ (B) $\left(\frac{dV}{dT}\right)_p = K$ (C) $\left(\frac{dT}{dV}\right)_p = K$ (D) $\left(\frac{1}{T} - \frac{V}{T^2}\right)_p = 0$

Q.36 Rate of diffusion of a gas is :

- (A) directly proportional to its density (B) directly proportional to its molecular mass
(C) directly proportional to the square of its molecular mass
(D) inversely proportional to the square root of its molecular mass

Q.37 Which of the following gases will have the highest rate of diffusion ?

- (A) O_2 (B) CO_2 (C) NH_3 (D) N_2

Q.38 "The total pressure exerted by a number of non-reacting gases is equal to the sum of partial pressures of the gases under the same conditions" is known as :

- (A) Boyle's law (B) Dalton's law (C) Avogadro's law (D) Charles' law

Q.39 Equal masses of methane and oxygen are mixed in an empty container at $25^\circ C$. The fraction of the total pressure exerted by oxygen is :

- (A) $\frac{1}{3}$ (B) $\frac{1}{2}$ (C) $\frac{2}{3}$ (D) $\frac{1}{3} \times \frac{273}{298}$

Q.40 Equal masses of methane and hydrogen are mixed in an empty container at $25^\circ C$. The fraction of the total pressure exerted by hydrogen is :

- (A) $\frac{1}{2}$ (B) $\frac{8}{9}$ (C) $\frac{1}{9}$ (D) $\frac{16}{17}$

Q.41 A gaseous mixture of 2 moles of A, 3 moles of B, 5 moles of C and 10 moles of D is contained in a vessel. Assuming that gases are ideal and the partial pressure of C is 1.5 atm, the total pressure is :

- (A) 3 atm (B) 6 atm (C) 9 atm (D) 15 atm

Q.42 50 mL of a gas A diffuse through a membrane in the same time as for the diffusion of 40 mL of gas B under identical conditions of pressure and temperature. If the molecular mass of A is 64, that of B would be :

- (A) 100 (B) 250 (C) 200 (D) 80

Q.43 3.2 g of oxygen (at. mass = 16) and 0.2 g of hydrogen (at. mass = 1) are placed in a 1.12 litre flask at $0^\circ C$. The total pressure of the gas mixture will be :

- (A) 1 atm (B) 2 atm (C) 3 atm (D) 4 atm

Q.44 If 4 g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions ?

- (A) 16 g (B) 1 g (C) $\frac{1}{4}$ g (D) 64 g

GASEOUS STATE

- Q.45** A closed vessel contains equal number of hydrogen and nitrogen molecules. The total pressure is 740 mm of Hg. If N_2 molecules are removed, the pressure would become/remains :
 (A) Double of 740 mm of Hg (B) One-ninth of 740 mm of Hg
 (C) Unchanged (D) One-half of 740 mm of Hg
- Q.46** Two sealed containers of same capacity at the same temperature are filled with 44 g of hydrogen gas in one and 44 g of CO_2 in the other. If the pressure of CO_2 is 1 atm, what is the pressure in the hydrogen container ?
 (A) 1 atm (B) zero atm (C) 22 atm (D) 44 atm
- Q.47** Equal masses of ethane and hydrogen are mixed in an empty container at $25^\circ C$. The fraction of the total pressure exerted by hydrogen is :
 (A) 1 : 2 (B) 1 : 1 (C) 1 : 16 (D) 15 : 16
- Q.48** A mixture contains 56 g of nitrogen, 44 g of CO_2 and 16 g of methane. The total pressure of the mixture is 720 mm Hg. The partial pressure of methane is :
 (A) 180 mm (B) 360 mm (C) 540 mm (D) 720 mm
- Q.49** If 100 mL of gas A at 600 torr and 500 mL of gas B at 800 torr are placed in a 2 litre flask, the final pressure will be :
 (A) 2000 torr (B) 1000 torr (C) 500 torr (D) 400 torr
- Q.50** A mixture of three gases X (density 1.0), Y (density 0.2) and Z (density 0.4) is enclosed in a vessel at constant temperature. When the equilibrium is established, the gas/gases :
 (A) X will be at the top of the vessel (B) Y will be at the top of the vessel
 (C) Z will be at the top of the vessel (D) Will mix homogeneously throughout the vessel
- Q.51** Which of the following mixture of gases at room temperature does not follow Dalton's law of partial pressures ?
 (A) NO_2 and O_2 (B) NH_3 and HCl (C) CO and CO_2 (D) SO_2 and O_2
- Q.52** In which of the following pairs the gaseous species diffuse through a porous plug along with the same rate of diffusion ?
 (A) NO, CO (B) NO, CO_2 (C) NH_3 , PH_3 (D) NO, C_2H_6
- Q.53** According to Graham's law at a given temperature, the ratio of the rates of diffusion r_A/r_B of gases A and B is given by :
 (A) $\frac{P_A}{P_B} \cdot \left(\frac{M_A}{M_B}\right)^{1/2}$ (B) $\frac{M_A}{M_B} \cdot \left(\frac{P_A}{P_B}\right)^{1/2}$ (C) $\frac{P_A}{P_B} \cdot \left(\frac{M_B}{M_A}\right)^{1/2}$ (D) $\frac{M_A}{M_B} \cdot \left(\frac{P_A}{P_B}\right)^{1/2}$

ANSWERS

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	D	D	A	A	B	B	C	A	A	C	C	B	B	D
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	D	B	C	D	A	A	D	B	C	D	D	C	C	A	B
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	C	C	C	C	B,C,D	D	C	B	A	A	B	A	D	B	D
Que.	46	47	48	49	50	51	52	53							
Ans.	C	D	A	C	D	B	D	C							

GASEOUS STATE

17. KINETIC THEORY OF GASES

17.1 The kinetic theory of gases gives an idealized model of a gas which can explain the behaviour of all gases-

17.2 Postulates of this theory are :

17.2.1 All gases consist of molecules, these molecules are extremely small hard spheres.

17.2.2 The molecules are in random rapid motion.

17.2.3 They travel in straight lines, collides with one another and with the walls of the container.

17.2.4 These collisions are perfectly elastic collisions. During such collisions there may be change in kinetic energy of the molecules (but there is no loss of mass).

17.2.5 The pressure of a gas is simply due to the force with which the molecules collide on the walls of the container.

17.2.6 The temperature of a gas is directly proportional to the average kinetic energy of the molecules.

17.2.7 In a given volume the number of molecules is very large, but the volume occupied by the gas molecules is negligible in comparison with the total volume of the gas, i.e. the volume of the container.

17.2.8 There are no forces of attraction or repulsion between molecules.

18. KINETIC GAS EQUATION

18.1 The above mentioned postulates help us in obtaining the fundamental kinetic gas equation :

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

Here P = pressure of gas,

V = volume of gas,

m = mass of each molecule,

n = total no. of molecules,

u = root mean square velocity of the molecule in cm s⁻¹.

for 1 mole of gas, m x N = mol. mass

Therefore the above equation can be written as

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

$$u = \sqrt{\frac{3PV}{M}} \quad \text{or} \quad \sqrt{\frac{3RT}{M}} \quad \text{or} \quad \sqrt{\frac{3p}{d}}$$

18.2 Calculation of Kinetic energy :-

According to gas equation

$$PV = \frac{1}{3} Mu^2 \quad \text{for 1 mole of gas}$$

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

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

GASEOUS STATE

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

$$\text{For 1 molecule, the K.E.} = \frac{3RT}{2N_0} = \frac{3}{2} KT$$

$$\frac{R}{N_0} = K \text{ (Boltzmann Constant)}$$

18.3 Gas Constant per molecule is known as Boltzmann Constant (K)

$$K = \frac{R}{N} = 1.38 \times 10^{-10} \text{ ergs / K / molecule}$$

$$\text{or } 1.38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1}$$

19. MOLECULAR COLLISIONS

19.1 The gaseous molecules undergo collisions with one another. At a given temperature the total number of collisions taking place in the unit volume of the gas per second is called collision frequency (Z).

19.2 For binary collisions it is mathematically expressed as

$$Z = \frac{1}{\sqrt{2}} \pi v \sigma^2 N^2$$

$$\text{Since } v = \frac{1}{\sqrt{2}} \pi \left(\frac{8RT}{\pi M} \right)^{1/2} \sigma^2 N^2 = 2 \sigma^2 N^2 \sqrt{\frac{\pi RT}{M}}$$

Here σ = molecular diameter,

v = average velocity

and N = number of molecules per unit volume

At particular temperature;

$$Z \propto P^2$$

At Particular pressure :

$$Z \propto T^{-3/2}$$

At particular volume ;

$$Z \propto T^{1/2}$$

19.3 During molecular collisions a molecule covers a small distance before it gets deflected.

19.4 The average distance travelled by the gas molecules between two successive collisions is called mean free Path (λ). It is mathematically expressed as

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 N}$$

$$\text{Since } \frac{N}{V} = \frac{P}{RT}$$

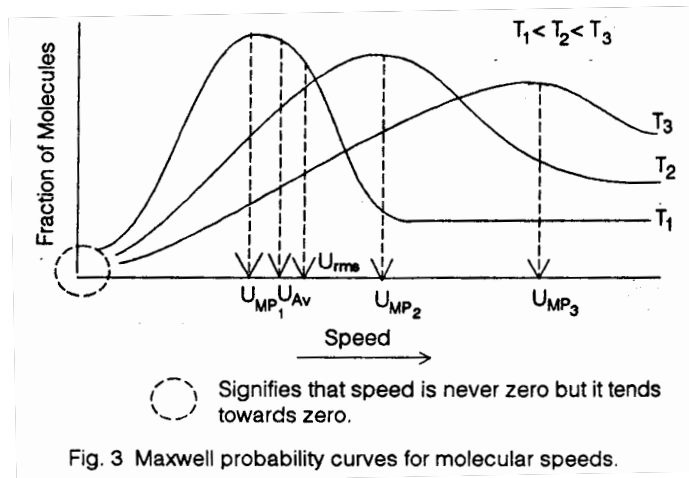
$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2} \cdot \frac{RT}{PV}$$

GASEOUS STATE

19.5 Thus at constant temperature the mean free path increases with the decrease in pressure and vice versa whereas, at constant pressure the mean free path increases with increase in temperature.

20. MOLECULAR SPEEDS

20.1 Due to frequent molecular collisions molecules do not possess same speed. According to Maxwell, the distribution of molecular speeds at a particular temperature is given by curve as shown



20.2 Some special features of the curve are : -

20.2.1 Fraction of molecules with too high or too low speeds is very small.

20.2.2 No molecule has zero velocity

20.2.3 Initially the fraction of molecules increases with increase in velocity reaches the peak of the curve which pertains to most probable velocity and thereafter it falls with increases in velocity.

21. MOLECULAR VELOCITIES

21.1 **Different types of velocities :** The three different types of velocity possessed by gas molecules are.

21.1.1 **Most probable velocity (α) :** It is the velocity possessed by the maximum fraction of the molecules of the gas at particular temperature -

$$\text{Mathematically } \alpha = \left(\frac{2RT}{M} \right)^{1/2}$$

21.1.2 **Average velocity (\bar{v}) :** It is arithmetic mean of the different velocities of the molecules of the gas at particular temperature.

$$\text{Mathematically } \bar{v} = \left[\frac{8RT}{\pi M} \right]^{1/2}$$

21.1.3 **Root mean square velocity (u) :** It is the square root of the average of the squares of the different velocities of the molecules at particular conditions.

$$\text{Mathematically } u = \left(\frac{3RT}{M} \right)^{1/2}$$

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21.2 The three types of velocities are related are

$$\bar{v} = 0.9213 u$$

$$\alpha = 0.816 \times u$$

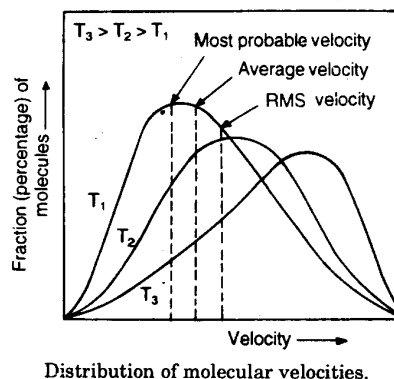
21.3 d : \bar{v} : u

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

$$\sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$1.414 : 1.595 : 1.732$$

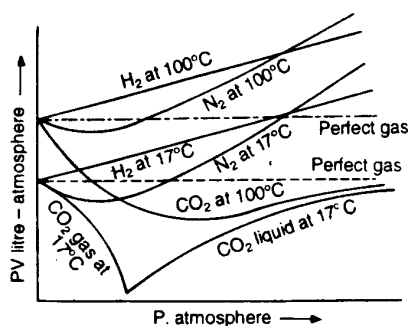
$$1 : 1.128 : 1.224$$



22. LIMITATIONS OF GAS EQUATION, PV = RT

22.1 At low temperature and high pressure wide deviations from this ideal behaviour occur.

22.2 Amagat, Andrew and Regnault Studied the effect of change of pressure on the volumes of hydrogen, nitrogen and carbon dioxide at different temperatures. The curves known as Amagat's curves are depicted in the Figure. For a perfect gas the curves should be straight line but it is either less or more deviated depending upon the nature of gas, temperature and pressure.



22.2.1 At low pressure the deviations are represented by the left hand ends of the curves. It is clear that PV for all gases except H₂ has lower value than expected for an ideal gas.

22.2.2 At higher pressure the deviations are indicated by the right hand ends of the curves. It is evident that PV for all gases has a higher value than expected for an ideal gas.

22.2.3 At low temperature the deviations are much more pronounced than at higher temperature.

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SOLVED EXAMPLES

Q.1 For two gases A and B with molecular weights M_A and M_B , it is observed that at a certain temperature T , the mean velocity of A is equal to the root mean square velocity of B. Thus the mean velocity of A can be made equal to the mean velocity of B, if :

- (A) A is at temperature T , and B at T' , $T > T'$.
- (B) A is lowered to a temperature $T_2 < T$ while B is at T
- (C) Both A and B are raised to a higher temperature
- (D) Both A and B are placed at lower temperature

Ans. (B)

$$u_{av - A} = \sqrt{\frac{8RT}{\pi M_A}} ;$$

$$u_{rms - B} = \sqrt{\frac{3RT}{M_B}}$$

$$\therefore \frac{8}{3\pi} = \frac{M_A}{M_B}$$

For $u_{av - A} = \sqrt{\frac{8RT_2}{\pi M_A}}$

$$u_{av - B} = \sqrt{\frac{8RT}{\pi M_B}}$$

$$\frac{T_2}{T} = \frac{M_A}{M_B} = \frac{8}{3\pi}$$

$$\therefore T_2 = \frac{8}{3\pi} \cdot T$$

or $T_2 < T$.

Q.2 If for two gases of molecular weights M_A and M_B at temperature T_A and T_B , $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases :

- (A) Density
- (B) Pressure
- (C) KE Per mol
- (D) *rms* velocity

Ans. (D)

Given $T_A \cdot M_B = T_B \cdot M_A$

or $\frac{T_A}{M_A} = \frac{T_B}{M_B}$

Also, $u_{rms} = \sqrt{\frac{3RT}{M}}$

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Q.3 At 0°C the average and total kinetic energy of 0.6 mol of an ideal gas are :

- (A) $3.405 \times 10^3 \text{ J mol}^{-1}$ and $2.043 \times 10^3 \text{ J}$ respectively
- (B) $4.805 \times 10^5 \text{ J mol}^{-1}$ and $4.508 \times 10^5 \text{ J}$ respectively
- (C) $0.0821 \times 10^3 \text{ J mol}^{-1}$ and $6.02 \times 10^3 \text{ J}$ respectively
- (D) $1.021 \times 10^3 \text{ J mol}^{-1}$ and $2.401 \times 10^3 \text{ J}$ respectively.

Ans. (A)

Average K.E. per mole of the gas is given by :

$$\begin{aligned} \text{K. E.} &= \frac{3}{2} RT \\ &= \frac{3}{2} (8.324 \text{ JK}^{-1} \text{ mol}^{-1}) (273 \text{ K}) \end{aligned}$$

Average K.E./mole = $3.405 \times 10^3 \text{ J mol}^{-1}$
and total K.E. of 0.6 mol of gas is :
 $= (0.6 \text{ mol}) (3.405 \times 10^3 \text{ J mol}^{-1})$
 $= 2.043 \times 10^3 \text{ J}.$

Q.4 Which of the following statement (s) is/are true :

- (A) Kinetic energy of a molecule is zero at 0°C.
- (B) Equal volume of gases contain equal numbers of moles.
- (C) Heat capacity of diatomic gas is higher than of monoatomic gas.
- (D) A gas in closed container exerts much higher pressure due to more gravity at the bottom than at the top.

Ans. (C)

$$C_p = \frac{5}{2} R \text{ for monoatomic gas}$$

$$C_p = \frac{7}{2} R \text{ for diatomic gas.}$$

Q.5 For the non zero volume of the molecules, ideal gas equation for 'n' mol of the gas will be :

- (A) $PV = nRT + nbP$
- (B) $P(V - b) = nRT$
- (C) $\left[P + \frac{a}{V^2} \right] V = RT$
- (D) (A) and (B) are correct.

Ans. (D)

Q.6 What is the pressure of HCl gas at -40°C if its density is 8.0 kg m^{-3} ? [$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$].

- (A) $42.458 \times 10^2 \text{ Pa}$
- (B) $424.58 \times 10^2 \text{ Pa}$
- (C) $424.58 \times 10^3 \text{ Pa}$
- (D) None of these

Sol. (C)

Equation for ideal gas,

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

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$$\begin{aligned} \text{or} \quad P &= \frac{w}{V} \times \frac{RT}{M} \\ &= d \times \frac{RT}{M} \quad \left(\frac{w}{V} = \text{density} = d \right) \end{aligned}$$

Substituting the values in the above equation,

$$P = \frac{8.0 \times 8.314 \times 233}{36.5 \times 10^{-3}} = 424.58 \times 10^3 \text{ Pa}$$

Q.7 The density of phosphorus vapour at 310°C and 775 torr is 2.64 g dm⁻³. What is the molecular formula of phosphorus ?

- (A) P₄ (B) P₈ (C) P₂ (D) P₆

Sol. (A)

$$\text{We know that } P = \frac{d}{M} RT \quad \text{or} \quad M = \frac{d}{P} RT$$

$$\text{Given, } d = 2.64 \text{ g dm}^{-3}; \quad p = \frac{775}{760} \text{ atm};$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$\text{and } T = 310 + 273 = 583 \text{ K}$$

$$\text{So } M = \frac{2.64 \times 0.0821 \times 583 \times 760}{775} = 123.9 \text{ g mol}^{-1}$$

$$\text{Atomic mass of P} = 31 \text{ g mol}^{-1}$$

$$\text{No. of P atoms in a molecule} = \frac{123.9}{31} = 3.997 \approx 4$$

Hence, Molecular formula of phosphorus = P₄

Q.8 The density of oxygen is 1.43 g L⁻¹ at STP. Determine the density of oxygen at 17°C and 800 torr.

- (A) 1.417 g L⁻¹ (B) 2.417 g L⁻¹ (C) 1.85 g L⁻¹ (D) 3.034 g L⁻¹

Sol. (A)

$$\text{Applying the formula } d = \frac{MP}{RT}$$

$$\text{At STP } d_1 = \frac{MP_1}{RT_1}$$

$$[P_1 = 760 \text{ torr}; T_1 = 273 \text{ K}; d_1 = 1.43 \text{ g L}^{-1}]$$

At given conditions

$$d_2 = \frac{MP_2}{RT_2} \quad [P_2 = 800 \text{ torr}; T_2 = 290\text{K}; d_2 = ?]$$

$$\text{So } \frac{d_2}{d_1} = \frac{P_2}{T_2} \times \frac{T_1}{P_1}$$

$$\begin{aligned} \text{or} \quad d_2 &= \frac{P_2}{P_1} \times \frac{T_1}{T_2} \times d_1 \\ &= \frac{800}{760} \times \frac{273}{290} \times 1.43 \\ &= 1.417 \text{ g L}^{-1} \end{aligned}$$

Ex.9 Internal energy and pressure of a gas per unit volume are related as -

(A) $P = \frac{2}{3} E$ (B) $P = \frac{3}{2} E$ (C) $P = \frac{1}{2} E$ (D) $P = 2E$

Sol. (A)

$$KE = \frac{3}{2} RT = \frac{3}{2} PV$$

$$\therefore P = \frac{2}{3} \frac{E}{V} \text{ [for unit volume } v = 1]$$

$$\therefore P = \frac{2}{3} E$$

Ex.10 According to kinetic theory of gases, for a diatomic molecule -

- (A) The pressure exerted by the gas is proportional to the mean velocity of the molecules.
- (B) Kinetic energy of the gas becomes zero and molecular motion also becomes zero at 0°C.
- (C) Kinetic energy of the gas decreases but does not become zero.
- (D) The mean translational kinetic energy of the molecules is proportional to the absolute temperature.

Sol. (D)

All molecules of an ideal gas show random motion They collide with each other and walls of container during which they lose or gain energy so they may not have some kinetic energy always.

Ex.11 Four molecules of a gas have speed of 1,2,3,4 cm, s⁻¹ respectively. The root mean square velocity is

(A) $\sqrt{7.5}$ (B) $\sqrt{30}$ (C) 30 (D) 0.15

Sol. (A)

$$u = \sqrt{\frac{1^2 + 2^2 + 3^2 + 4^2}{4}} = \sqrt{\frac{30}{4}} = \sqrt{7.5}$$

Ex.12 The temperature at which RMS velocity of SO₂ molecules is half that of He molecules at 300 K is

(A) 150 K (B) 600 K (C) 900 K (D) 1200 K

Sol. (D)

As Root Mean Square velocity. $\mu = \sqrt{\frac{3RT}{M}}$

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$$\text{Hence. } \frac{\mu(\text{SO}_2)}{\mu(\text{He})} = \sqrt{\frac{T(\text{SO}_2)}{M(\text{SO}_2)} \times \frac{M(\text{He})}{T(\text{He})}}$$

$$\frac{1}{2} = \sqrt{\frac{T(\text{SO}_2)}{64} \times \frac{4}{300}}$$

$$T(\text{SO}_2) = \frac{64 \times 300}{4 \times 4} = 1200 \text{ K}$$

Ex.13 The rate of diffusion of two gases x and y is in the ratio of 1 : 5 and that of y and z in the ratio 1 : 6
The ratio of the rate of diffusion of z with respect to x is :

- (A) 5/6 (B) 1/30 (C) 6/5 (D) 30

Sol. (B)

$$\frac{r_x}{r_y} = \frac{1}{5} \quad , \quad \frac{r_y}{r_z} = \frac{1}{6}.$$

$$\text{Multiplying } \frac{r_x}{r_z} = \frac{1}{30} \text{ or } \frac{r_z}{r_x} = 30.$$

UNSOLVED PROBLEMS

- Q.1** According to kinetic theory of gases :
(A) There are intermolecular attractions (B) molecules have considerable volume
(C) there is no intramolecular attraction (D) speed of molecules decreases for each collision
- Q.2** Postulate of kinetic theory is :
(A) atom is indivisible (B) gases combine in simple ratio
(C) there is no influence of gravity on the molecules of the gas
(D) none of the above
- Q.3** Which of the following statements is not consistent with the postulates of kinetic theory of gases ?
(A) Gases consist of large number of tiny particles
(B) Particles are in constant motion
(C) All the particles have same speed
(D) Pressure is due to hits recorded by particles against the walls of containing vessel
- Q.4** A helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of helium atom is :
(A) two times that of a hydrogen molecule (B) four times that of a hydrogen molecule
(C) half that of a hydrogen molecule (D) same as that of a hydrogen molecule
- Q.5** The kinetic theory of gases predicts that total kinetic energy of a gas depends on :
(A) pressure of the gas (B) temperature of the gas
(C) volume of the gas (D) pressure, temperature and volume of the gas

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- Q.6** If a gas is allowed to expand at constant temperature then :
(A) number of molecules of the gas decreases
(B) the kinetic energy of the gas molecules decreases
(C) the kinetic energy of the gas molecules increases
(D) the kinetic energy of the gas molecules remains the same
- Q.7** Gases deviate from ideal behaviour because molecules :
(A) are colourless (B) are spherical (C) attract each other (D) have high speeds
- Q.8** In a closed vessel, a gas is heated from 300 K to 600 K; the kinetic energy becomes/remains :
(A) double (B) half (C) same (D) four times
- Q.9** The root mean square speed of an ideal gas at 27°C is 0.3 m/sec. Its RMS velocity at 927°C is :
(A) 3.0 m/sec (B) 2.4 m/sec (C) 0.9 m/sec (D) 0.6 m/sec
- Q.10** The RMS speed at NTP of the species can be calculated from the expression :
(A) $\sqrt{\frac{3P}{d}}$ (B) $\sqrt{\frac{3PV}{M}}$ (C) $\sqrt{\frac{3RT}{M}}$ (D) all
- Q.11** At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to :
(A) increase in average molecular speed (B) increased rate of collisions amongst molecules
(C) increased in molecular attraction (D) decrease in mean free path
- Q.12** The ratio of root mean square speed and average speed of a gas molecule, at a particular temperature, is :
(A) 1 : 1.086 (B) 1.086 : 1 (C) 2 : 1.086 (D) 1.086 : 2
- Q.13** Most probable speed, average speed and RMS speed are related as :
(A) 1 : 1.224 : 1.128 (B) 1.128 : 1 : 1.224 (C) 1 : 1.128 : 1.224 (D) 1.224 : 1.128 : 1
- Q.14** In a closed flask of 5 litre, 1.0 g of H₂ is heated from 300-600 K. Which statement is not correct ?
(A) The rate of collision increases (B) The energy of gaseous molecules increases
(C) The number of mole of the gas increases (D) Pressure of the gas increases
- Q.15** The root mean square speed is expressed as :
(A) $\left[\frac{3}{2}RT\right]^{1/2}$ (B) $\left[\frac{2RT}{M}\right]^{1/2}$ (C) $\left[\frac{3RT}{M}\right]$ (D) $\left[\frac{3RT}{M}\right]^{1/2}$
- Q.16** The RMS speed of hydrogen molecules at room temperature is 2400 m s⁻¹. At room temperature the RMS speed of oxygen molecules would be :
(A) 400 m s⁻¹ (B) 300 m s⁻¹ (C) 600 m s⁻¹ (D) 1600 m s⁻¹
- Q.17** The molecules of which of the following gas have highest speed ?
(A) Hydrogen at -50°C (B) Methane at 298 K (C) Nitrogen at 1000°C (D) Oxygen at 0°C

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- Q.18** Which one of the following is an ideal gas ?
 (A) Hydrogen (B) Nitrogen (C) Carbon dioxide (D) None
- Q.19** Two samples of gases A and B are at the same temperature. The molecules of 'A' are travelling four times faster than the molecules of B. The ratio of m_A/m_B of their masses will be :
 (A) 16 (B) 4 (C) 1/4 (D) 1/16
- Q.20** The root mean square speed of a certain gas at 27°C is $3 \times 10^4 \text{ cm s}^{-1}$. The temperature at which the velocity will be $6 \times 10^4 \text{ cm s}^{-1}$ is :
 (A) 54°C (B) 108°C (C) 1200 K (D) 600 K
- Q.21** According to kinetic theory of gases for a di-atomic molecule :
 (A) the pressure exerted by the gas is proportional to the mean square speed of the molecules
 (B) the pressure exerted by the gas is proportional to the root mean square speed of the molecules
 (C) the root mean square speed is inversely proportional to the temperature
 (D) the mean translational K.E. of the molecule is directly proportional to the absolute temperature
- Q.22** When an ideal gas undergoes unrestricted expansion, no cooling occurs because the molecules :
 (A) exert no attractive forces on each other (B) do work equal to loss of kinetic energy
 (C) collide without loss of energy (D) are above the inversion temperature
- Q.23** Which of the following statements is correct ?
 (A) $3PV = mnc^2$ is the expression for real gases
 (B) At normal temperature and pressure most gases behave nearly as ideal gases
 (C) The molecules of real gases have both volume and mutual attraction
 (D) Pressure depends on number of molecules and volume
- Q.24** At STP, the order of mean square velocity of molecules of H_2 , N_2 , O_2 and HBr is :
 (A) $\text{H}_2 > \text{N}_2 > \text{O}_2 > \text{HBr}$ (B) $\text{HBr} > \text{O}_2 > \text{N}_2 > \text{H}_2$
 (C) $\text{HBr} > \text{H}_2 > \text{O}_2 > \text{N}_2$ (D) $\text{N}_2 > \text{O}_2 > \text{H}_2 > \text{HBr}$
- Q.25** If the universal gas constant is $8.3 \text{ joule mol}^{-1} \text{ K}^{-1}$ and the Avogadro's number 6×10^{23} . The mean kinetic energy of the oxygen molecules at 327°C will be :
 (A) $415 \times 10^{-23} \text{ joule}$ (B) $2490 \times 10^{-22} \text{ joule}$ (C) $1245 \times 10^{-23} \text{ joule}$ (D) $830 \times 10^{-22} \text{ joule}$
- Q.26** At what temperature would be RMS speed of a gas molecule have twice its value at 100°C ?
 (A) 4192 K (B) 1492 K (C) 9142 K (D) 2491 K
- Q.27** The root mean square velocity of an ideal gas at constant pressure varies with density as :
 (A) d^2 (B) d (C) \sqrt{d} (D) $\frac{1}{\sqrt{d}}$

ANSWERS

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	C	C	D	B	D	C	A	D	D	A	B	C	C	D
Que.	16	17	18	19	20	21	22	23	24	25	26	27			
Ans.	C	A	D	B	C	D	A	C	A	C	B	D			