Kinetic Theory of Gases

Introduction

In gases the intermolecular forces are very weak and its molecule may fly apart in all directions. So the gas is characterised by the following properties.

(i) It has no shape and size and can be obtained in a vessel of any shape or size.
(ii) It expands indefinitely and uniformly to fill the available space.
(iii) It exerts pressure on its surroundings.

Assumption of Kinetic Theory of Gases

Kinetic theory of gases relates the macroscopic properties of gases (such as pressure, temperature *etc.*) to the microscopic properties of the gas molecules (such as speed, momentum, kinetic energy of molecule *etc.*)

Actually it attempts to develop a model of the molecular behaviour which should result in the observed behaviour of an ideal gas. It is based on following assumptions :

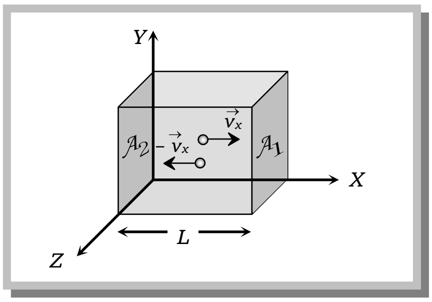
(1) Every gas consists of extremely small particles known as molecules. The molecules of a given gas are all identical but are different than those of another gas.
(2) The molecules of a gas are identical, spherical, rigid and perfectly elastic point masses.
(3) Their size is negligible in comparison to intermolecular distance (10^{-9} m)
(4) The volume of molecules is negligible in comparison to the volume of gas. (The volume of molecules is only 0.014% of the volume of the gas).
(5) Molecules of a gas keep on moving randomly in all possible direction with all possible velocities.
(6) The speed of gas molecules lie between zero and infinity (very high speed).
(7) The number of molecules moving with most probable speed is maximum.
(8) The gas molecules keep on colliding among themselves as well as with the walls of containing vessel. These collisions are perfectly elastic. (*i.e.* the total energy before collision = total energy after the collision).
(9) Molecules move in a straight line with constant speeds during successive collisions.
(10) The distance covered by the molecules between two successive collisions is known as free path and mean of all free paths is known as mean free path.
(11) The time spent *M* a collision between two molecules is negligible in comparison to time between two successive collisions.
(12) The number of collisions per unit volume in a gas remains constant.
(13) No attractive or repulsive force acts between gas molecules.
(14) Gravitational attraction among the molecules is ineffective due to extremely small masses and very high speed of molecules.
(15) Molecules constantly collide with the walls of container due to which their momentum changes. The change in momentum is transferred to the walls of the container. Consequently pressure is exerted by gas molecules on the walls of container.
(16) The density of gas is constant at all points of the container.

Pressure of an Ideal Gas

Consider an ideal gas (consisting of N molecules each of mass m) enclosed in a cubical box of side L.

It's any molecule moves with velocity $\vec{v}$ in any direction where $\vec{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}$

This molecule collides with the shaded wall (A_1) with velocity v_x and rebounds with velocity $-v_x$.



The change in momentum of the molecule $\Delta P = (-mv_x) - (mv_x) = -2mv_x$

As the momentum remains conserved in a collision, the change in momentum of the wall A_1 is $\Delta P = 2mv_x$

After rebound this molecule travel toward opposite wall A_2 with velocity $-v_x$, collide to it and again rebound with velocity v_x towards wall A_1.

(1) Time between two successive collision with the wall A_1.

$$\Delta t = \frac{\text{Distance travelled by molecule between two successive collision}}{\text{Velocity of molecule}} = \frac{2L}{v_x}$$

$\therefore$ Number of collision per second $n = \frac{1}{\Delta t} = \frac{v_x}{2L}$

(2) The momentum imparted per unit time to the wall by this molecule $n\Delta P = \frac{v_x}{2L} 2mv_x = \frac{m}{L}v_x^2$

This is also equal to the force exerted on the wall A_1 due to this molecule $\therefore$ $\Delta F = \frac{m}{L}v_x^2$

(3) The total force on the wall A_1 due to all the molecules $F_x = \frac{m}{L}\sum v_x^2$

(4) Now pressure is defined as force per unit area

$\therefore$ $P_x = \frac{F_x}{A} = \frac{m}{AL}\sum v_x^2 = \frac{m}{V}\sum v_x^2$ Similarly $P_y = \frac{m}{V}\sum v_y^2$ and $P_z = \frac{m}{V}\sum v_z^2$

So $P_x + P_y + P_z = \frac{m}{V}\sum (v_x^2 + v_y^2 + v_z^2)$

$3P = \frac{m}{V}\sum v^2$ [As $P_x = P_y = P_z = P$ and $v^2 = v_x^2 + v_y^2 + v_z^2$]

$3P = \frac{m}{V}(v_1^2 + v_2^2 + v_3^3 + ...)$

or $3P = \frac{mN}{V}\left(\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + ...}{N}\right)$

or $3P = \frac{m\,N}{V}v_{rms}^2$ [As root mean square velocity of the gas molecule $v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + ...}{N}}$]

or $P = \frac{1}{3}\frac{m\,N}{V}v_{rms}^2$

Important points

(i) $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$ or $P \propto \frac{(mN)T}{V}$ [As $v_{rms}^2 \propto T$]

(a) If volume and temperature of a gas are constant $P \propto mN$ *i.e.* Pressure $\propto$ (Mass of gas).

i.e. if mass of gas is increased, number of molecules and hence number of collision per second increases *i.e.* pressure will increase.

(b) If mass and temperature of a gas are constant. $P \propto (1/V)$, *i.e.*, if volume decreases, number of collisions per second will increase due to lesser effective distance between the walls resulting in greater pressure.

(c) If mass and volume of gas are constant, $P \propto (v_{rms})^2 \propto T$

i.e., if temperature increases, the mean square speed of gas molecules will increase and as gas molecules are moving faster, they will collide with the walls more often with greater momentum resulting in greater pressure.

(ii) $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2 = \frac{1}{3}\frac{M}{V}v_{rms}^2$ [As $M = mN$ = Total mass of the gas]

$\therefore$ $P = \frac{1}{3}\rho v_{rms}^2$ $\left[\text{As } \rho = \frac{M}{V}\right]$

(iii) Relation between pressure and kinetic energy

Kinetic energy $= \frac{1}{2}Mv_{rms}^2$

$\therefore$ Kinetic energy per unit volume $(E) = \frac{1}{2}\left(\frac{M}{V}\right)v_{rms}^2 = \frac{1}{2}\rho v_{rms}^2$ .....(i)

and we know $P = \frac{1}{3}\rho v_{rms}^2$ .....(ii)

From (i) and (ii), we get $P = \frac{2}{3}E$

i.e. the pressure exerted by an ideal gas is numerically equal to the two third of the mean kinetic energy of translation per unit volume of the gas.

Sample Problems based on Pressure

Problem 1. The root mean square speed of hydrogen molecules of an ideal hydrogen gas kept in a gas chamber at 0°*C* is 3180 *m/s*. The pressure on the hydrogen gas is

(Density of hydrogen gas is $8.99 \times 10^{-2}\ kg/m^3$, 1 atmosphere $= 1.01 \times 10^5\ N/m^2$)

(a) 0.1 *atm* (b) 1.5 *atm* (c) 2.0 *atm* (d) 3.0 *atm*

Solution : (d) As $P = \frac{1}{3}\rho v_{\text{rms}}^2 = \frac{1}{3}(8.99 \times 10^{-2}) \times (3180)^2 = 3.03 \times 10^5\ N/m^2 = 3.0\, atm$

Problem 2. The temperature of a gas is raised while its volume remains constant, the pressure exerted by a gas on the walls of the container increases because its molecules

(a) Lose more kinetic energy to the wall

(b) Are in contact with the wall for a shorter time

(c) Strike the wall more often with higher velocities

(d) Collide with each other less frequency

Solution : (c) Due to increase in temperature root mean square velocity of gas molecules increases. So they strike the wall more often with higher velocity. Hence the pressure exerted by a gas on the walls of the container increases.

Problem 3. A cylinder of capacity 20 *litres* is filled with H_2 gas. The total average kinetic energy of translatory motion of its molecules is $1.5\times10^5\ J$. The pressure of hydrogen in the cylinder is

(a) $2\times10^6\ N/m^2$ (b) $3\times10^6\ N/m^2$ (c) $4\times10^6\ N/m^2$ (d) $5\times10^6\ N/m^2$

Solution : (d) Kinetic energy E = $1.5\times10^5\ J$, volume V = 20 *litre* = $20\times10^{-3} m^3$

Pressure $= \frac{2}{3}\frac{E}{V} = \frac{2}{3}\left(\frac{1.5\times10^5}{20\times10^{-3}}\right) = 5\times10^6\ N/m^2$.

Problem 4. N molecules each of mass m of gas A and $2N$ molecules each of mass $2m$ of gas B are contained in the same vessel at temperature T. The mean square of the velocity of molecules of gas B is v^2 and the mean square of x component of the velocity of molecules of gas A is w^2. The ratio $\frac{w^2}{v^2}$ is

(a) 1 (b) 2 (c) $\frac{1}{3}$ (d) $\frac{2}{3}$

Solution : (d) Mean square velocity of molecule $= \frac{3kT}{m}$

For gas A, x component of mean square velocity of molecule $= w^2$

$\therefore$ Mean square velocity $= 3w^2 = \frac{3kT}{m}$ .....(i)

For B gas mean square velocity $= v^2 = \frac{3kT}{2m}$ .....(ii)

From (i) and (ii) $\frac{3w^2}{v^2} = \frac{2}{1}$ so $\frac{w^2}{v^2} = \frac{2}{3}$.

Problem 5. A flask contains $10^{-3} m^3$ gas. At a temperature, the number of molecules of oxygen are 3.0×10^{22}. The mass of an oxygen molecule is $5.3\times10^{-26} kg$ and at that temperature the *rms* velocity of molecules is 400 *m/s*. The pressure in N/m^2 of the gas in the flask is

(a) 8.48×10^4 (b) 2.87×10^4 (c) 25.44×10^4 (d) 12.72×10^4

Solution : (a) $V = 10^{-3} m^3$, $N = 3.0\times10^{22}$, $m = 5.3\times10^{-26} kg$, $v_{rms} = 400\ m/s$

$$P = \frac{1}{3}\frac{mN}{V}v_{rms}^2 = \frac{1}{3}\times\frac{5.3\times10^{-26}\times3.0\times10^{22}}{10^{-3}}(400)^2 = 8.48\times10^4\ N/m^2.$$

***Problem* 6.** A gas at a certain volume and temperature has pressure 75 *cm*. If the mass of the gas is doubled at the same volume and temperature, its new pressure is

(a) 37.5 *cm* (b) 75 *cm* (c) 150 *cm* (d) 300 *cm*

Solution : (c) $P = \frac{1}{3}\frac{M}{V}v_{rms}^2 \quad \therefore \; P \propto \frac{MT}{V}$

At constant volume and temperature, if the mass of the gas is doubled then pressure will become twice.

Ideal Gas Equation

A gas which strictly obeys the gas laws is called as perfect or an ideal gas. The size of the molecule of an ideal gas is zero *i.e.* each molecule is a point mass with no dimension. There is no force of attraction or repulsion amongst the molecule of the gas. All real gases are not perfect gases. However, at extremely low pressure and high temperature, the gases like hydrogen, nitrogen, helium *etc.* are nearly perfect gases.

The equation which relates the pressure (P), volume (V) and temperature (T) of the given state of an ideal gas is known as gas equation.

Ideal gas equations	
For 1 mole or N_A molecule or M gram or 22.4 *litres* of gas	$PV = RT$
For μ mole of gas	$PV = \mu RT$
For 1 molecule of gas	$PV = \left(\frac{R}{N_A}\right)T = kT$
For N molecules of gas	$PV = NkT$
For 1 *gm* of gas	$PV = \left(\frac{R}{M}\right)T = rT$
for n *gm* of gas	$PV = nrT$

(1) **Universal gas constant (*R*) :** Dimension $[ML^2T^{-2}\theta^{-1}]$

$$R = \frac{PV}{\mu T} = \frac{\text{Pressure} \times \text{Volume}}{\text{No. of moles} \times \text{Temperature}} = \frac{\text{Work done}}{\text{No. of moles} \times \text{Temperature}}$$

Thus universal gas constant signifies the work done by (or on) a gas per mole per kelvin.

S.T.P. value : $8.31 \frac{Joule}{mole \times kelvin} = 1.98 \frac{cal}{mole \times kelvin} = 0.8221 \frac{litre \times atm}{mole \times kelvin}$

(2) **Boltzman's constant (*k*) :** Dimension $[ML^2T^{-2}\theta^{-1}]$

$$k = \frac{R}{N} = \frac{8.31}{6.023 \times 10^{23}} = 1.38 \times 10^{-23} \; Joule/kelvin$$

(3) **Specific gas constant (*r*) :** Dimension $[L^2T^{-2}\theta^{-1}]$

$r = \frac{R}{M}$; Unit : $\frac{Joule}{gm \times kelvin}$

Since the value of M is different for different gases. Hence the value of r is different for different gases.

Sample Problems based on Ideal gas equation

Problem 7. A gas at 27°C has a volume V and pressure P. On heating its pressure is doubled and volume becomes three times. The resulting temperature of the gas will be

(a) 1800°C (b) 162°C (c) 1527°C (d) 600°C

Solution : (c) From ideal gas equation $PV = \mu RT$ we get $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)\left(\frac{V_2}{V_1}\right) = \left(\frac{2P_1}{P_1}\right)\left(\frac{3V_1}{V_1}\right) = 6$

$\therefore\ T_2 = 6T_1 = 6 \times 300 = 1800\ K = 1527\,°C.$

Problem 8. A balloon contains $500\,m^3$ of helium at 27°C and 1 atmosphere pressure. The volume of the helium at – 3°C temperature and 0.5 atmosphere pressure will be

(a) $500\ m^3$ (b) $700\ m^3$ (c) $900\ m^3$ (d) $1000\ m^3$

Solution : (c) From $PV = \mu RT$ we get $\frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right) = \left(\frac{270}{300}\right)\left(\frac{1}{0.5}\right) = \frac{9}{5} \Rightarrow V_2 = 500 \times \frac{9}{5} = 900\ m^3$

Problem 9. When volume of system is increased two times and temperature is decreased half of its initial temperature, then pressure becomes

(a) 2 times (b) 4 times (c) 1 / 4 times (d) 1 / 2 times

Solution : (c) From $PV = \mu RT$ we get $\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{T_1/2}{T_1}\right)\left(\frac{V_1}{2V_1}\right) = \frac{1}{4} \Rightarrow P_2 = \frac{P_1}{4}$

Problem 10. The equation of state corresponding to 8g of O_2 is

(a) $PV = 8RT$ (b) $PV = RT/4$ (c) $PV = RT$ (d) $PV = RT/2$

Solution : (b) As 32 *gm* O_2 means 1 *mole* therefore 8 *gm* O_2 means 1 / 4*mole i.e.* $\mu = \frac{1}{4}$

So from $PV = \mu RT$ we get $PV = \frac{1}{4}RT$ or $PV = \frac{RT}{4}$

Problem 11. A flask is filled with 13 *gm* of an ideal gas at 27°C and its temperature is raised to 52°C. The mass of the gas that has to be released to maintain the temperature of the gas in the flask at 52°C and the pressure remaining the same is

(a) 2.5 g (b) 2.0 g (c) 1.5 g (d) 1.0 g

Solution : (d) $PV \propto$ Mass of gas × Temperature

In this problem pressure and volume remains constant so $M_1T_1 = M_2T_2$ = constant

$\therefore\ \frac{M_2}{M_1} = \frac{T_1}{T_2} = \frac{(27+273)}{(52+273)} = \frac{300}{325} = \frac{12}{13} \Rightarrow M_2 = M_1 \times \frac{12}{13} = 13 \times \frac{12}{13}\,gm = 12\,gm$

i.e. the mass of gas released from the flask = 13 *gm* – 12 *gm* = 1 *gm*.

Problem 12. Air is filled at 60°C in a vessel of open mouth. The vessel is heated to a temperature T so that 1 / 4th part of air escapes. Assuming the volume of vessel remaining constant, the value of T is

(a) 80°C (b) 444°C (c) 333°C (d) 171°C

Solution : (d) $M_1 = M,\ T_1 = 60 + 273 = 333\ K,\ M_2 = M - \frac{M}{4} = \frac{3M}{4}$ [As 1 / 4th part of air escapes]

If pressure and volume of gas remains constant then MT = constant

$\therefore\ \frac{T_2}{T_1} = \frac{M_1}{M_2} = \left(\frac{M}{3M/4}\right) = \frac{4}{3} \Rightarrow T_2 = \frac{4}{3} \times T_1 = \frac{4}{3} \times 333 = 444\ K = 171\,°C$

Problem 13. If the intermolecular forces vanish away, the volume occupied by the molecules contained in 4.5 *kg* water at standard temperature and pressure will be given by

(a) $5.6\,m^3$ (b) $4.5\,m^3$ (c) 11.2 *litre* (d) $11.2\,m^3$

Solution : (a) $\mu = \frac{\text{Mass of water}}{\text{Molecular wt. of water}} = \frac{4.5\,kg}{18\times 10^{-3}\,kg} = 250$, $T = 273\ K$ and $P = 10^5\ N/m^2$ (STP)

From $PV = \mu RT \Rightarrow V = \frac{\mu RT}{P} = \frac{250\times 8.3\times 273}{10^5} = 5.66\,m^3$.

Problem 14. The pressure *P*, volume *V* and temperature *T* of a gas in the jar *A* and the other gas in the jar *B* at pressure 2*P*, volume *V*/4 and temperature 2*T*, then the ratio of the number of molecules in the jar *A* and *B* will be

(a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 4 : 1

Solution : (d) Ideal gas equation $PV = \mu RT = \left(\frac{N}{N_A}\right)RT$ where N = Number of molecule, N_A = Avogadro number

$$\therefore \frac{N_1}{N_2} = \left(\frac{P_1}{P_2}\right)\left(\frac{V_1}{V_2}\right)\left(\frac{T_2}{T_1}\right) = \left(\frac{P}{2P}\right)\left(\frac{V}{V/4}\right)\left(\frac{2T}{T}\right) = \frac{4}{1}.$$

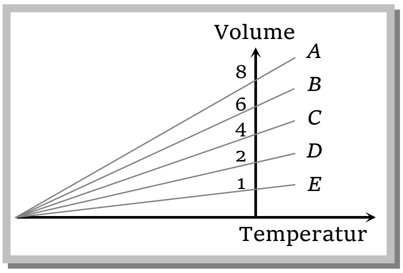
Problem 15. The expansion of an ideal gas of mass *m* at a constant pressure *P* is given by the straight line *D*. Then the expansion of the same ideal gas of mass 2*m* at a pressure *P*/ 2 is given by the straight line

(a) *E*

(b) *C*

(c) *B*

(d) *A*



Solution : (d) From $PV \propto MT$ or $V \propto \frac{M}{P}T$; Here $\left(\frac{M}{P}\right)$ represents the slope of curve drawn on volume and temperature axis.

For first condition slope $\left(\frac{M}{P}\right)$ graph is *D* (given in the problem)

For second condition slope $\frac{2M}{P/2} = 4\left(\frac{M}{P}\right)$ *i.e.* slope becomes four time so graph *A* is correct in this condition.

Problem 16. If the value of molar gas constant is 8.3 *J/mole-K*, the *n* specific gas constant for hydrogen in *J/mole-K* will be

(a) 4.15 (b) 8.3 (c) 16.6 (d) None of these

Solution : (a) Specific gas constant $r = \frac{\text{Universal gas constant }(R)}{\text{Molecular weight of gas }(M)} = \frac{8.3}{2} = 4.15$ *Joule/mole-K*.

Problem **17.** A gas in container A is in thermal equilibrium with another gas in container B. both contain equal masses of the two gases in the respective containers. Which of the following can be true

(a) $P_AV_A = P_BV_B$ (b) $P_A = P_B, V_A \neq V_B$ (c) $P_A \neq P_B, V_A = V_B$ (d) $\frac{P_A}{V_A} = \frac{P_B}{V_B}$

Solution : (b, c) According to problem mass of gases are equal so number of moles will not be equal *i.e.* $\mu_A \neq \mu_B$

From ideal gas equation $PV = \mu RT \;\therefore\; \frac{P_AV_A}{\mu_A} = \frac{P_BV_B}{\mu_B}$

[As temperature of the container are equal]

From this relation it is clear that if $P_A = P_B$ then $\frac{V_A}{V_B} = \frac{\mu_A}{\mu_B} \neq 1$ *i.e.* $V_A \neq V_B$

Similarly if $V_A = V_B$ then $\frac{P_A}{P_B} = \frac{\mu_A}{\mu_B} \neq 1$ *i.e.* $P_A \neq P_B$.

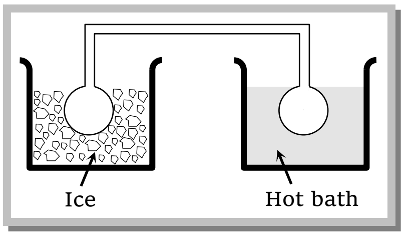
Problem **18.** Two identical glass bulbs are interconnected by a thin glass tube. A gas is filled in these bulbs at N.T.P. If one bulb is placed in ice and another bulb is placed in hot bath, then the pressure of the gas becomes 1.5 times. The temperature of hot bath will be

(a) 100°C

(b) 182°C

(c) 256°C

(d) 546°C



Solution : (d) Quantity of gas in these bulbs is constant *i.e.* Initial No. of moles in both bulb = final number of moles

$$\mu_1 + \mu_2 = \mu_1' + \mu_2'$$

$$\frac{PV}{R(273)} + \frac{PV}{R(273)} = \frac{1.5\,PV}{R(273)} + \frac{1.5PV}{R(T)} \Rightarrow \frac{2}{273} = \frac{1.5}{273} + \frac{1.5}{T}$$

$$\Rightarrow T = 819\,K = 546°C.$$

Problem **19.** Two containers of equal volume contain the same gas at pressures P_1 and P_2 and absolute temperatures T_1 and T_2 respectively. On joining the vessels, the gas reaches a common pressure P and common temperature T. The ratio P/T is equal to

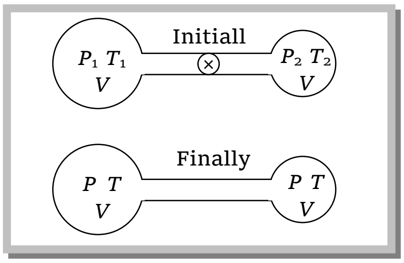
(a) $\frac{P_1}{T_1} + \frac{P_2}{T_2}$ (b) $\frac{P_1T_1 + P_2T_2}{(T_1 + T_2)^2}$ (c) $\frac{P_1T_2 + P_2T_1}{(T_1 + T_2)^2}$ (d) $\frac{P_1}{2T_1} + \frac{P_2}{2T_2}$

Solution : (d) Number of moles in first vessel $\mu_1 = \frac{P_1V}{RT_1}$ and number of moles in second vessel $\mu_2 = \frac{P_2V}{RT_2}$

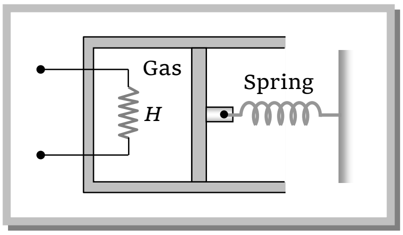
If both vessels are joined together then quantity of gas remains same *i.e* $\mu = \mu_1 + \mu_2$

$$\frac{P(2V)}{RT} = \frac{P_1V}{RT_1} + \frac{P_2V}{RT_2}$$

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



Problem 20. An ideal monoatomic gas is confined in a cylinder by a spring-loaded piston if cross-section $8 \times 10^{-3}\, m^2$. Initially the gas is at 300*K* and occupies a volume of $2.4 \times 10^{-3}\, m^3$ and the spring is in a relaxed state. The gas is heated by a small heater coil *H*. The force constant of the spring is 8000 *N*/*m*, and the atmospheric pressure is $1.0 \times 10^5\, Pa$. The cylinder and piston are thermally insulated. The piston and the spring are massless and there is no friction between the piston and cylinder. There is no heat loss through heater coil wire leads and thermal capacity of the heater coil is negligible. With all the above assumptions, if the gas is heated by the heater until the piston moves out slowly by 0.1*m*, then the final temperature is



(a) 400 *K*

(b) 800 *K*

(c) 1200 *K*

(d) 300 *K*

Solution : (b) $V_1 = 2.4 \times 10^{-3}\, m^3$, $P_1 = P_0 = 10^5 \dfrac{N}{m^2}$ and T_1 = 300 *K* (given)

If area of cross-section of piston is *A* and it moves through distance *x* then increment in volume of the gas = *Ax*

and if force constant of a spring is *k* then force *F* = *kx* and pressure = $\dfrac{F}{A} = \dfrac{kx}{A}$

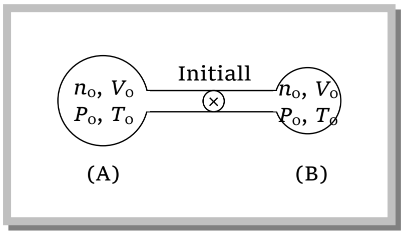
$V_2 = V_1 + Ax = 2.4 \times 10^{-3} + 8 \times 10^{-3} \times 0.1 = 3.2 \times 10^{-3}$ and $P_2 = P_0 + \dfrac{kx}{A} = 10^5 + \dfrac{8000 \times 0.1}{8 \times 10^{-3}} = 2 \times 10^5$

From ideal gas equation $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2} \Rightarrow \dfrac{10^5 \times 2.4 \times 10^{-3}}{300} = \dfrac{2 \times 10^5 \times 3.2 \times 10^{-3}}{T_2} \Rightarrow T_2 = 800\, K$

Problem 21. Two identical containers each of volume V_0 are joined by a small pipe. The containers contain identical gases at temperature T_0 and pressure P_0. One container is heated to temperature $2T_0$ while maintaining the other at the same temperature. The common pressure of the gas is *P* and *n* is the number of moles of gas in container at temperature $2T_0$

(a) $P = 2P_0$ (b) $P = \dfrac{4}{3} P_0$ (c) $n = \dfrac{2}{3} \dfrac{P_0 V_0}{RT_0}$ (d) $n = \dfrac{3}{2} \dfrac{P_0 V_0}{RT_0}$

Solution : (b, c) Initially for container *A* $P_0 V_0 = n_0 RT_0$

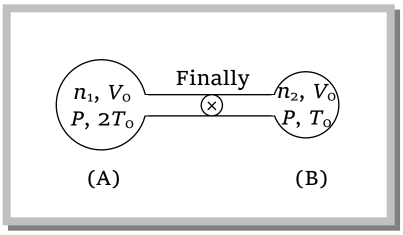


For container *B* $P_0 V_0 = n_0 RT_0 \quad \therefore\ n_0 = \dfrac{P_0 V_0}{RT_0}$

Total number of moles $= n_0 + n_0 = 2n_0$

Since even on heating the total number of moles is conserved

Hence $n_1 + n_2 = 2n_0$ ......(i)



If *P* be the common pressure then

For container *A* $PV_0 = n_1 R 2T_0 \quad \therefore\ n_1 = \dfrac{PV_0}{2RT_0}$

For container *B* $PV_0 = n_2 RT_0 \quad \therefore n_2 = \dfrac{PV_0}{RT_0}$

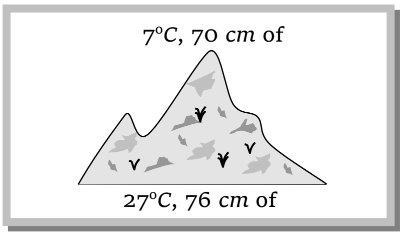
Substituting the value of n_0, n_1 and n_2 in equation (i)

we get $\dfrac{PV_0}{2RT_0} + \dfrac{PV_0}{RT_0} = \dfrac{2.P_0 V_0}{RT_0} \Rightarrow P = \dfrac{4}{3} P_0$

No. of moles in container A (at temperature $2T_0$) = $n_1 = \frac{PV_0}{2RT_0} = \left(\frac{4}{3}P_0\right)\frac{V_0}{2RT_0} = \frac{2}{3}\frac{P_0V_0}{RT_0}$

$\left[\text{As } P = \frac{4}{3}P_0\right]$

***Problem* 22.** At the top of a mountain a thermometer reads 7°C and a barometer reads 70 cm of Hg. At the bottom of the mountain these read 27°C and 76 cm of Hg respectively. Comparison of density of air at the top with that of bottom is



(a) 75/76

(b) 70/76

(c) 76/75

(d) 76/70

Solution : (a) Ideal gas equation, in terms of density $\frac{P_1}{\rho_1 T_1} = \frac{P_2}{\rho_2 T_2} = \text{constant}$ $\therefore \frac{\rho_1}{\rho_2} = \frac{P_1}{P_2} \times \frac{T_2}{T_1}$

$$\therefore \frac{\rho_{\text{Top}}}{\rho_{\text{Bottom}}} = \frac{P_{\text{Top}}}{P_{\text{Bottom}}} \times \frac{T_{\text{Bottom}}}{T_{\text{Top}}} = \frac{70}{76} \times \frac{300}{280} = \frac{75}{76}$$

Vander Waal's Gas Equation

All real gases do not obey the ideal gas equation. In order to explain the behaviour of real gases following two modification are considered in ideal gas equation.

(i) **Non-zero size of molecule:** A certain portion of volume of a gas is covered by the molecules themselves. Therefore the space available for the free motion of molecules of gas will be slightly less than the volume V of a gas.

Hence the effective volume becomes $(V - b)$

(ii) **Force of attraction between gas molecules:** Due to this, molecule do not exert that force on the wall which they would have exerted in the absence of intermolecular force. Therefore the observed pressure P of the gas will be less than that present in the absence of intermolecular force. Hence the effective pressure becomes $\left(P + \frac{a}{V^2}\right)$

The equation obtained by using above modifications in ideal gas equation is called Vander Waal's equation or real gas equation.

Vander Waal's gas equations	
For 1 *mole* of gas	$\left(P + \frac{a}{V^2}\right)(V - b) = RT$
For μ *moles* of gas	$\left(P + \frac{a\mu^2}{V^2}\right)(V - \mu b) = \mu RT$

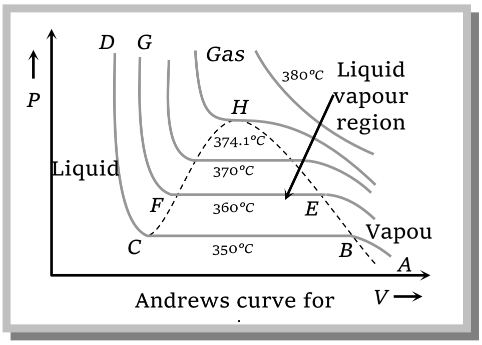
Here a and b are constant called Vander Waal's constant.

Dimension : $[a] = [ML^5T^{-2}]$ and $[b] = [L^3]$

Units : $a = N \times m^4$ and $b = m^3$.

Andrews Curves

The pressure (P) versus volume (V) curves for actual gases are called Andrews curves.



Andrews curve for

(1) At 350°C, part AB represents vapour phase of water, in this part Boyle's law is obeyed $\left(P \propto \frac{1}{V}\right)$. Part BC represents the co-existence of vapour and liquid phases. At point C, vapours completely change to liquid phase. Part CD is parallel to pressure axis which shows that compressibility of the water is negligible.

(2) At 360°C portion representing the co-existence of liquid vapour phase is shorter.

(3) At 370°C this portion is further decreased.

(4) At 374.1°C, it reduces to point (H) called critical point and the temperature 374.1°C is called critical temperature (T_c) of water.

(5) The phase of water (at 380°C) above the critical temperature is called gaseous phase.

Critical temperature, pressure and volume

The point on the P-V curve at which the matter gets converted from gaseous state to liquid state is known as critical point. At this point the difference between the liquid and vapour vanishes *i.e.* the densities of liquid and vapour become equal.

(i) **Critical temperature (T_c):** The maximum temperature below which a gas can be liquefied by pressure alone is called critical temperature and is characteristic of the gas. A gas cannot be liquefied if its temperature is more than critical temperature.

CO_2 (304.3 K), O_2 (−118°C), N_2 (−147.1°C) and H_2O (374.1°C)

(ii) **Critical pressure (P_c):** The minimum pressure necessary to liquify a gas at critical temperature is defined as critical pressure.

CO_2 (73.87 bar) and O_2 (49.7atm)

(iii) **Critical volume (V_c):** The volume of 1 mole of gas at critical pressure and critical temperature is defined as critical volume.

CO_2 ($95 \times 10^{-6}\ m^3$)

(iv) **Relation between Vander Waal's constants and T_c, P_c, V_c :**

$$T_c = \frac{8a}{27Rb},\quad P_c = \frac{a}{27b^2},\quad V_c = 3b,\qquad a = \frac{27R^2}{64}\frac{T_c^2}{P_c},\quad b = \frac{R}{8}\left(\frac{T_c}{P_c}\right) \quad \text{and} \quad \frac{P_c V_c}{T_c} = \frac{3}{8}R$$

Sample problems based on Vander Waal gas equation

Problem 23. Under which of the following conditions is the law $PV = RT$ obeyed most closely by a real gas

(a) High pressure and high temperature (b) Low pressure and low temperature

(c) Low pressure and high temperature (d) High pressure and low temperature

Solution : (c) At low pressure and high temperature real gas obey $PV = RT$ *i.e.* they behave as ideal gas because at high temperature we can assume that there is no force of attraction or repulsion works among the molecules and the volume occupied by the molecules is negligible in comparison to the volume occupied by the gas.

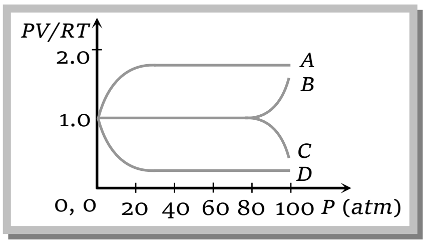
Problem 24. The equation of state of a gas is given by $\left(P + \frac{aT^2}{V}\right)V^c = (RT + b)$, where a, b, c and R are constants. The isotherms can be represented by $P = AV^m - BV^n$, where A and B depend only on temperature then

(a) $m = -c$ and $n = -1$ (b) $m = c$ and $n = 1$ (c) $m = -c$ and $n = 1$ (d) $m = c$ and $n = -1$

Solution : (a) $\left(P + \frac{aT^2}{V}\right)V^c = RT + b \Rightarrow P + aT^2V^{-1} = RTV^{-c} + bV^{-c} \Rightarrow P = (RT + b)V^{-c} - (aT^2)V^{-1}$

By comparing this equation with given equation $P = AV^m - BV^n$ we get $m = -c$ and $n = -1$.

Problem 25. An experiment is carried on a fixed amount of gas at different temperatures and at high pressure such that it deviates from the ideal gas behaviour. The variation of $\frac{PV}{RT}$ with P is shown in the diagram. The correct variation will correspond to



(a) Curve A

(b) Curve B

(c) Curve C

(d) Curve D

Solution : (b) At lower pressure we can assume that given gas behaves as ideal gas so $\frac{PV}{RT}$ = constant but when pressure increase, the decrease in volume will not take place in same proportion so $\frac{PV}{RT}$ will increases.

Problem 26. The conversion of ideal gas into solids is

(a) Possible only at low pressure (b) Possible only at low temperature

(c) Possible only at low volume (d) Impossible

Solution : (d) Because there is zero attraction between the molecules of ideal gas.

Various Speeds of Gas Molecules

The motion of molecules in a gas is characterised by any of the following three speeds.

(1) **Root mean square speed :** It is defined as the square root of mean of squares of the speed of different molecules *i.e.* $v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + \dots}{N}}$

(i) From the expression for pressure of ideal gas $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$

$$v_{rms} = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3PV}{\text{Mass of gas}}} = \sqrt{\frac{3P}{\rho}} \qquad \left[\text{As } \rho = \frac{\text{Mass of gas}}{V}\right]$$

(ii) $v_{rms} = \sqrt{\frac{3PV}{\text{Mass of gas}}} = \sqrt{\frac{3\mu RT}{\mu M}} = \sqrt{\frac{3RT}{M}}$ [As if M is the molecular weight of gas

(iii) $v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3N_A kT}{N_A M}} = \sqrt{\frac{3kT}{m}}$ [As $M = N_A m$ and $R = N_A k$]

$\therefore$ Root mean square velocity $v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$

Important points

(i) With rise in temperature *rms* speed of gas molecules increases as $v_{rms} \propto \sqrt{T}$.

(ii) With increase in molecular weight *rms* speed of gas molecule decreases as $v_{rms} \propto \frac{1}{\sqrt{M}}$.

e.g., *rms* speed of hydrogen molecules is four times that of oxygen molecules at the same temperature.

(iii) *rms* speed of gas molecules is of the order of *km/s*

e.g., At NTP for hydrogen gas $(v_{rms}) = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 273}{2 \times 10^{3}}} = 1840\ m/s$.

(iv) *rms* speed of gas molecules is $\sqrt{\frac{3}{\gamma}}$ times that of speed of sound in gas

As $v_{rms} = \sqrt{\frac{3RT}{M}}$ and $v_s = \sqrt{\frac{\gamma RT}{M}}$ $\therefore$ $v_{rms} = \sqrt{\frac{3}{\gamma}}v_s$

(v) *rms* speed of gas molecules does not depends on the pressure of gas (if temperature remains constant) because $P \propto \rho$ (Boyle's law) if pressure is increased *n* times then density will also increases by *n* times but v_{rms} remains constant.

(vi) Moon has no atmosphere because v_{rms} of gas molecules is more than escape velocity (v_e).

A planet or satellite will have atmosphere only and only if $v_{rms} < v_e$

(vii) At $T = 0$; $v_{rms} = 0$ *i.e.* the *rms* speed of molecules of a gas is zero at 0 *K*. This temperature is called absolute zero.

(2) **Most probable speed:** The particles of a gas have a range of speeds. This is defined as the speed which is possessed by maximum fraction of total number of molecules of the gas. *e.g.*, if speeds of 10 molecules of a gas are 1, 2, 2, 3, 3, 3, 4, 5, 6, 6 *km/s*, then the most probable speed is 3 *km/s*, as maximum fraction of total molecules possess this speed.

Most probable speed $v_{mp} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$

(3) **Average speed:** It is the arithmetic mean of the speeds of molecules in a gas at given temperature.

$$v_{av} = \frac{v_1 + v_2 + v_3 + v_4 + ...}{N}$$

and according to kinetic theory of gases

Average speed $v_{av} = \sqrt{\frac{8P}{\pi\rho}} = \sqrt{\frac{8}{\pi}\frac{RT}{M}} = \sqrt{\frac{8}{\pi}\frac{kT}{m}}$

Note : ❑ $v_{rms} > v_{av} > v_{mp}$ (order remembering trick) (RAM)

❑ $v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = \sqrt{3} : \sqrt{2.5} : \sqrt{2}$

❑ For oxygen gas molecules v_{rms} = 461 *m/s*, v_{av} = 424.7 *m/s* and v_{rms} = 376.4 *m/s*

Sample Problems based on Various speeds

Problem **27.** At room temperature, the *rms* speed of the molecules of certain diatomic gas is found to be 1930 *m/s*. The gas is

(a) H_2 (b) F_2 (c) O_2 (d) Cl_2

Solution : (a) Root means square velocity $v_{rms} = \sqrt{\frac{3RT}{M}} = 1930\ m/s$ (given)

$\therefore\ M = \frac{3RT}{(1930)^2} = \frac{3 \times 8.31 \times 300}{1930 \times 1930} = 2 \times 10^{-3}\ kg = 2\ gm$ *i.e.* the gas is hydrogen.

Problem **28.** Let *A* and *B* the two gases and given : $\frac{T_A}{M_A} = 4.\frac{T_B}{M_B}$; where *T* is the temperature and *M* is the molecular mass. If C_A and C_B are the *rms* speed, then the ratio $\frac{C_A}{C_B}$ will be equal to

(a) 2 (b) 4 (c) 1 (d) 0.5

Solution : (a) As $v_{rms} = \sqrt{\frac{3RT}{M}}$ $\therefore\ \frac{C_A}{C_B} = \sqrt{\frac{T_A / T_B}{M_A / M_B}} = \sqrt{4} = 2$ $\left[\text{As} \frac{T_A}{T_B} = 4\frac{M_A}{M_B} \text{given}\right]$

Problem **29.** The *rms* speed of the molecules of a gas in a vessel is 400 ms^{-1}. If half of the gas leaks out at constant temperature, the *rms* speed of the remaining molecules will be

(a) 800 ms^{-1} (b) $400\sqrt{2}\ ms^{-1}$ (c) 400 ms^{-1} (d) 200 ms^{-1}

Solution : (c) Root mean square velocity does not depends upon the quantity of gas. For a given gas and at constant temperature it always remains same.

__Problem__ **30.** The root mean square speed of hydrogen molecules at 300 *K* is 1930 *m/s*. Then the root mean square speed of oxygen molecules at 900 *K* will be

(a) $1930\sqrt{3}\, m/s$ (b) 836 *m/s* (c) 643 *m/s* (d) $\frac{1930}{\sqrt{3}} m/s$

Solution : (b) $v_{rms} = \sqrt{\frac{3RT}{M}}$ $\therefore$ $\frac{v_{H_2}}{v_{O_2}} = \sqrt{\frac{T_{H_2}}{M_{H_2}} \times \frac{M_{O_2}}{T_{O_2}}}$

$\Rightarrow \frac{1930}{v_{O_2}} = \sqrt{\frac{300}{2} \times \frac{32}{900}} \Rightarrow v_{O_2} = \frac{1930 \times \sqrt{3}}{4} = 836\, m/s$.

__Problem__ **31.** At what temperature is the root mean square velocity of gaseous hydrogen molecules is equal to that of oxygen molecules at 47°*C*

(a) 20 *K* (b) 80 *K* (c) – 73 *K* (d) 3 *K*

Solution : (a) For oxygen $v_{O_2} = \sqrt{\frac{3RT_{O_2}}{M_{O_2}}}$ and For hydrogen $v_{H_2} = \sqrt{3R\frac{T_{H_2}}{M_{H_2}}}$

According to problem $= \sqrt{\frac{3RT_{O_2}}{M_{O_2}}} = \sqrt{3R\frac{T_{H_2}}{M_{H_2}}}$

$\Rightarrow \frac{T_{O_2}}{M_{O_2}} = \frac{T_{H_2}}{M_{H_2}} \Rightarrow \frac{47+273}{32} = \frac{T_{H_2}}{2} \Rightarrow T_{H_2} = \frac{320}{32} \times 2 = 20\, K$.

__Problem__ **32.** Cooking gas containers are kept in a lorry moving with uniform speed. The temperature of the gas molecules inside will

(a) Increase (b) Decrease

(c) Remain same (d) Decrease for some, while increase for others

Solution : (c) If a lorry is moving with constant velocity then the v_{rms} of gas molecule inside the container will not change and we know that $T \propto v_{rms}^2$. So temperature remains same.

__Problem__ **33.** The speeds of 5 molecules of a gas (in arbitrary units) are as follows : 2, 3, 4, 5, 6. The root mean square speed for these molecules is

(a) 2.91 (b) 3.52 (c) 4.00 (d) 4.24

Solution : (d) $v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2 + v_5^2}{5}} = \sqrt{\frac{2^2 + 3^2 + 4^2 + 5^2 + 6^2}{5}} = \sqrt{\frac{100}{5}} = \sqrt{20} = 4.24$

__Problem__ **34.** Gas at a pressure P_0 in contained as a vessel. If the masses of all the molecules are halved and their speeds are doubled, the resulting pressure *P* will be equal to

(a) $4P_0$ (b) $2P_0$ (c) P_0 (d) $\frac{P_0}{2}$

Solution : (b) $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$ $\therefore$ $P \propto m v_{rms}^2$ so $\frac{P_2}{P_1} = \frac{m_2}{m_1} \times \left(\frac{v_2}{v_1}\right)^2 = \frac{m_1/2}{m_1}\left(\frac{2v_1}{v_1}\right)^2 = 2 \Rightarrow P_2 = 2P_1 = 2P_0$

Problem **35.** Let $\bar{v}, v_{rms}$ and v_{mp} respectively denote the mean speed, root mean square speed and most probable speed of the molecules in an ideal monoatomic gas at absolute temperature *T*. The mass of a molecule is *m*. Then

(a) No molecule can have speed greater than $\sqrt{2}\, v_{rms}$

(b) No molecule can have speed less than $v_{mp}/\sqrt{2}$

(c) $v_{mp} < \bar{v} < v_{rms}$

(d) The average kinetic energy of a molecule is $\frac{3}{4} m v_{mp}^2$

Solution : (c, d) We know that $v_{rms} = \sqrt{\frac{3RT}{M}}$, $v_{av} = \sqrt{\frac{8}{\pi}\frac{RT}{M}}$ and $v_{mp} = \sqrt{2\frac{RT}{M}}$

$\therefore \quad v_{rms} : v_{av} : v_{mp} = \sqrt{3} : \sqrt{2.5} : \sqrt{2}$ so $v_{mp} < v_{av} < v_{rms}$

and $\frac{v_{rms}}{v_{mp}} = \sqrt{\frac{3}{2}}$ or $v_{rms}^2 = \frac{3}{2} v_{mp}^2$ $\quad \therefore$ Average kinetic energy $= \frac{1}{2} m v_{rms}^2 = \frac{1}{2} m \frac{3}{2} v_{mp}^2 = \frac{3}{4} m v_{mp}^2$.

Problem **36.** The root mean square speed of the molecules of a diatomic gas is *v*. When the temperature is doubled, the molecules dissociate into two atoms. The new root mean square speed of the atom is

(a) $\sqrt{2}v$ (b) *v* (c) 2*v* (d) 4*v*

Solution : (c) $v_{rms} = \sqrt{\frac{3RT}{M}}$. According to problem *T* will becomes *T*/2 and *M* will becomes *M*/2 so the value of v_{rms} will increase by $\sqrt{4} = 2$ times *i.e.* new root mean square velocity will be 2*v*.

Problem **37.** The molecules of a given mass of a gas have a *rms* velocity of 200 *m/sec* at 27°*C* and $1.0 \times 10^5\ N/m^2$ pressure. When the temperature is 127°*C* and pressure is $0.5 \times 10^5\ N/m^2$, the *rms* velocity in *m/sec* will be

(a) $\frac{100\sqrt{2}}{3}$ (b) $100\sqrt{2}$ (c) $\frac{400}{\sqrt{3}}$ (d) None of these

Solution : (c) Change in pressure will not affect the *rms* velocity of molecules. So we will calculate only the effect of temperature.

As $v_{rms} \propto \sqrt{T}$ $\quad \therefore \frac{v_{300^o}}{v_{400^o}} = \sqrt{\frac{300}{400}} = \sqrt{\frac{3}{4}} \Rightarrow \frac{200}{v_{400}} = \sqrt{\frac{3}{4}} \Rightarrow v_{400} = \frac{200 \times 2}{\sqrt{3}} = \frac{400}{\sqrt{3}} m/s$.

Problem **38.** Which of the following statement is true

(a) Absolute zero degree temperature is not zero energy temperature

(b) Two different gases at the same temperature pressure have equal root mean square velocities

(c) The *rms* speed of the molecules of different ideal gases, maintained at the same temperature are the same

(d) Given sample of 1*cc* of hydrogen and 1*cc* of oxygen both at N.T.P.; oxygen sample has a large number of molecules

Solution : (a) At absolute temperature kinetic energy of gas molecules becomes zero but they possess potential energy so we can say that absolute zero degree temperature is not zero energy temperature.

Problem 39. The ratio of *rms* speeds of the gases in the mixture of nitrogen oxygen will be

(a) 1 : 1 (b) $\sqrt{3}:1$ (c) $\sqrt{8}:\sqrt{7}$ (d) $\sqrt{6}:\sqrt{7}$

Solution : (c) $v_{rms} = \sqrt{\frac{3RT}{M}}$ $\therefore$ $\frac{v_{N_2}}{v_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{N_2}}} = \sqrt{\frac{32}{28}} = \sqrt{\frac{8}{7}}$

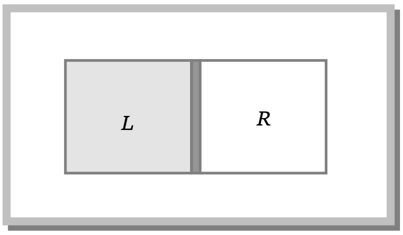
Problem 40. A vessel is partitioned in two equal halves by a fixed diathermic separator. Two different ideal gases are filled in left (L) and right (R) halves. The *rms* speed of the molecules in L part is equal to the mean speed of molecules in the R part. Then the ratio of the mass of a molecule in L part to that of a molecule in R part is

(a) $\sqrt{\frac{3}{2}}$

(b) $\sqrt{\pi/4}$

(c) $\sqrt{2/3}$

(d) $3\pi/8$



Solution : (d) Root means square velocity of molecule in left part $v_{rms} = \sqrt{\frac{3KT}{m_L}}$

Mean or average speed of molecule in right part $v_{av} = \sqrt{\frac{8}{\pi}\frac{KT}{m_R}}$

According to problem $\sqrt{\frac{3KT}{m_L}} = \sqrt{\frac{8}{\pi}\frac{KT}{m_R}} \Rightarrow \frac{3}{m_L} = \frac{8}{\pi m_R} \Rightarrow \frac{m_L}{m_R} = \frac{3\pi}{8}$.

Problem 41. An ideal gas (γ = 1.5) is expanded adiabatically. How many times has the gas to be expanded to reduce the root mean square velocity of molecules 2 times

(a) 4 times (b) 16 times (c) 8 times (d) 2 times

Solution : (b) To reduce the *rms* velocity two times, temperature should be reduced by four times (As $v_{rms} \propto \sqrt{T}$)

$\therefore$ $T_1 = T$ $T_2 = \frac{T}{4}$, $V_1 = V$

From adiabatic law $TV^{\gamma-1}$ = constant we get $\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_1}{T_2} = 4$

$\Rightarrow \frac{V_2}{V_1} = (4)^{\frac{1}{\gamma-1}}$ [γ = 3/2 given]

$\Rightarrow V_2 = V_1(4)^{\frac{1}{3/2-1}} = V_1(4)^2 = 16\,V_1$ $\therefore$ $\frac{V_2}{V_1} = 16$

Kinetic Energy of Ideal Gas

Molecules of ideal gases possess only translational motion. So they possess only translational kinetic energy.

Quantity of gas	Kinetic energy
Kinetic energy of a gas molecule ($E_{molecule}$)	$=\frac{1}{2}mv_{rms}^2 = \frac{1}{2}m\left(\frac{3kT}{m}\right) = \frac{3}{2}kT$ $\left[\text{As}\, v_{rms}\sqrt{\frac{3kT}{m}}\right]$
Kinetic energy of 1 *mole* (*M gram*) gas (E_{mole})	$=\frac{1}{2}Mv_{rms}^2 = \frac{1}{2}M\frac{3RT}{M} = \frac{3}{2}RT$ $\left[\text{As}\, v_{rms} = \sqrt{\frac{3RT}{M}}\right]$
Kinetic energy of 1 *gm* gas (E_{gram})	$=\frac{3}{2}\frac{R}{M}T = \frac{3}{2}\frac{kN_A}{mN_A}T = \frac{3}{2}\frac{k}{m}T = \frac{3}{2}rT$

Here m = mass of each molecule, M = Molecular weight of gas and N_A = Avogadro number = 6.023×10^{23}

Important points

(1) Kinetic energy per molecule of gas does not depends upon the mass of the molecule but only depends upon the temperature of the gas.

As $E = \frac{3}{2}kT$ or $E \propto T$ i.*e*. molecules of different gases say *He*, H_2 and O_2 *etc*. at same temperature will have same translational kinetic energy though their *rms* speed are different. $\left[v_{rms} = \sqrt{\frac{3kT}{m}}\right]$

(2) Kinetic energy per mole of gas depends only upon the temperature of gas.

(3) Kinetic energy per *gram* of gas depend upon the temperature as well as molecular weight (or mass of one molecule) of the gas.

$$E_{gram} = \frac{3}{2}\frac{k}{m}T \qquad \therefore\ E_{gram} \propto \frac{T}{m}$$

From the above expressions it is clear that higher the temperature of the gas, more will be the average kinetic energy possessed by the gas molecules at $T = 0$, $E = 0$ *i.e.* at absolute zero the molecular motion stops.

Sample Problems based on Kinetic energy

Problem **42.** Read the given statements and decide which is/are correct on the basis of kinetic theory of gases

(I) Energy of one molecule at absolute temperature is zero

(II) *rms* speeds of different gases are same at same temperature

(III) For one gram of all ideal gas kinetic energy is same at same temperature

(IV) For one mole of all ideal gases mean kinetic energy is same at same temperature

(a) All are correct (b) I and IV are correct (c) IV is correct (d) None of these

Solution : (c) If the gas is not ideal then its molecule will possess potential energy. Hence statement (I) is wrong.

rms speed of different gases at same temperature depends on its molecular weight $\left(v_{rms} \propto \frac{1}{\sqrt{M}}\right)$. Hence statement (II) also wrong.

Kinetic energy of one *gram* gas depends on the molecular weight $\left(E_{gm} \propto \frac{1}{M}\right)$. Hence statement (III) also wrong.

But K.E. of one mole of ideal gas does not depends on the molecular weight $\left(E = \frac{3}{2}RT\right)$. Hence (IV) is correct.

Problem **43.** At which of the following temperature would the molecules of a gas have twice the average kinetic energy they have at 20°C

(a) 40°C (b) 80°C (c) 313°C (d) 586°C

Solution : (c) $E \propto T \quad \therefore \frac{E_2}{E_1} = \frac{T_2}{T_1} \Rightarrow \frac{2E_1}{E_1} = \frac{T_2}{(20+273)} \Rightarrow T_2 = 293 \times 2 = 586\,K = 313°C$.

Problem **44.** A vessel contains a mixture of one mole of oxygen and two moles of nitrogen at 300 K. The ratio of the average rotational kinetic energy per O_2 molecule to that per N_2 molecule is

(a) 1 : 1

(b) 1 : 2

(c) 2 : 1

(d) Depends on the moments of inertia of the two molecules

Solution : (a) Kinetic energy per degree of freedom $= \frac{1}{2}kT$

As diatomic gas possess two degree of freedom for rotational motion therefore rotational K.E. $= 2\left(\frac{1}{2}kT\right) = kT$

In the problem both gases (oxygen and nitrogen) are diatomic and have same temperature (300 K) therefore ratio of average rotational kinetic energy will be equal to one.

Problem 45. A gas mixture consists of molecules of type 1, 2 and 3 with molar masses $m_1 > m_2 > m_3$. v_{rms} and $\overline{K}$ are the *rms* speed and average kinetic energy of the gases. Which of the following is true

(a) $(v_{rms})_1 < (v_{rms})_2 < (v_{rms})_3$ and $(\overline{K})_1 = (\overline{K})_2 = (\overline{K})_3$ (b) $(v_{rms})_1 = (v_{rms})_2 = (v_{rms})_3$ and $(\overline{K})_1 = (\overline{K})_2 > (\overline{K})_3$

(c) $(v_{rms})_1 > (v_{rms})_2 > (v_{rms})_3$ and $(\overline{K})_1 < (\overline{K})_2 > (\overline{K})_3$ (d) $(v_{rms})_1 > (v_{rms})_2 > (v_{rms})_3$ and $(\overline{K})_1 < (\overline{K})_2 < (\overline{K})_3$

Solution : (a) The *rms* speed depends upon the molecular mass $v_{rms} \propto \frac{1}{\sqrt{M}}$ but kinetic energy does not depends on it $E \propto M^0$

In the problem $m_1 > m_2 > m_3$ $\therefore$ $(v_{rms})_1 < (v_{rms})_2 < (v_{rms})_3$ but $(\overline{K}_1) = (\overline{K}_2) = (\overline{K}_3)$

Problem 46. The kinetic energy of one gram mole of a gas at normal temperature and pressure is (R = 8.31 *J/mole-K*)

(a) $0.56 \times 10^4 J$ (b) $1.3 \times 10^2 J$ (c) $2.7 \times 10^2 J$ (d) $3.4 \times 10^3 J$

Solution : (d) $E = \frac{3}{2}RT = \frac{3}{2} \times 8.31 \times 273 = 3.4 \times 10^3$ *Joule*

Problem 47. The average translational kinetic energy of O_2 (molar mass 32) molecules at a particular temperature is 0.048 *eV*. The translational kinetic energy of N_2 (molar mass 28) molecules in *eV* at the same temperature is

(a) 0.0015 (b) 0.003 (c) 0.048 (d) 0.768

Solution : (c) Average translational kinetic energy does not depends upon the molar mass of the gas. Different gases will possess same average translational kinetic energy at same temperature.

Problem 48. The average translational energy and the *rms* speed of molecules in a sample of oxygen gas at 300 *K* are $6.21 \times 10^{-21} J$ and 484 *m/s* respectively. The corresponding values at 600 *K* are nearly (assuming ideal gas behaviour)

(a) $12.42 \times 10^{-21} J, 968 m/s$ (b) $8.78 \times 10^{-21} J, 684 m/s$

(c) $6.21 \times 10^{-21} J, 968 m/s$ (d) $12.42 \times 10^{-21} J, 684 m/s$

Solution : (d) $E \propto T$ but $v_{rms} \propto \sqrt{T}$

i.e. if temperature becomes twice then energy will becomes two time *i.e.* $2 \times 6.21 \times 10^{-21} = 12.42 \times 10^{-21} J$

But *rms* speed will become $\sqrt{2}$ times *i.e.* $484 \times \sqrt{2} = 684$ *m/s*.

Problem 49. A box containing N molecules of a perfect gas at temperature T_1 and pressure P_1. The number of molecules in the box is doubled keeping the total kinetic energy of the gas same as before. If the new pressure is P_2 and temperature T_2, then

(a) $P_2 = P_1$, $T_2 = T_1$ (b) $P_2 = P_1$, $T_2 = \frac{T_1}{2}$ (c) $P_2 = 2P_1$, $T_2 = T_1$ (d) $P_2 = 2P_1$, $T_2 = \frac{T_1}{2}$

Solution : (b) Kinetic energy of N molecule of gas $E = \frac{3}{2}NkT$

Initially $E_1 = \frac{3}{2}N_1kT_1$ and finally $E_2 = \frac{3}{2}N_2kT_2$

But according to problem $E_1 = E_2$ and $N_2 = 2N_1$ $\therefore \frac{3}{2}N_1kT_1 = \frac{3}{2}(2N_1)kT_2 \Rightarrow T_2 = \frac{T_1}{2}$

Since the kinetic energy constant $\frac{3}{2}N_1kT_1 = \frac{3}{2}N_2kT_2 \Rightarrow N_1T_1 = N_2T_2$ $\therefore$ NT = constant

From ideal gas equation of N molecule $PV = NkT$

$\Rightarrow$ $P_1V_1 = P_2V_2$ $\therefore$ $P_1 = P_2$ [As $V_1 = V_2$ and NT = constant]

Problem **50.** Three closed vessels *A*, *B* and *C* are at the same temperature *T* and contain gases which obey the Maxwellian distribution of velocities. Vessel *A* contains only O_2, *B* only N_2 and *C* a mixture of equal quantities of O_2 and N_2. If the average speed of the O_2 molecules in vessel *A* is V_1, that of the N_2 molecules in vessel *B* is V_2, the average speed of the O_2 molecules in vessel *C* is (where *M* is the mass of an oxygen molecule)

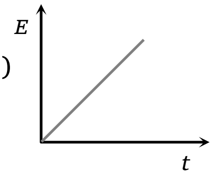
(a) $(V_1 + V_2)/2$ (b) V_1 (c) $(V_1V_2)^{1/2}$ (d) $\sqrt{3kT/M}$

Solution : (b) Average speed of gas molecule $v_{av} = \sqrt{\frac{8kT}{\pi m}}$. It depends on temperature and molecular mass.

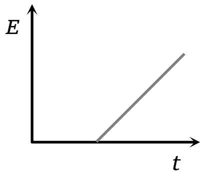
So the average speed of oxygen will be same in vessel *A* and vessel *C* and that is equal to V_1.

Problem **51.** The graph which represent the variation of mean kinetic energy of molecules with temperature *t*°*C* is

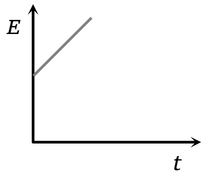
(a)



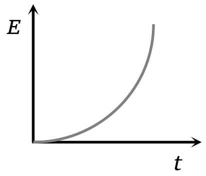
(b)



(c)



(d)



Solution : (c) Mean K.E. of gas molecule $E = \frac{3}{2}kT = \frac{3}{2}k(t + 273)$ where *T* = temperature is in kelvin and *t* = is in centigrade

$$\therefore \quad E = \frac{3}{2}k\,t + \frac{3}{2} \times 273\,k \qquad k = \text{Boltzmann's constant}$$

By comparing this equation with standard equation of straight line $y = mx + c$

We get $m = \frac{3}{2}k$ and $c = \frac{3}{2}273k$. So the graph between *E* and *t* will be straight line with positive intercept on *E*-axis and positive slope with *t*-axis.

Gas Laws

(1) **Boyle's law:** For a given mass of an ideal gas at constant temperature, the volume of a gas is inversely proportional to its pressure.

i.e. $V \propto \frac{1}{P}$ or PV = constant or $P_1V_1 = P_2V_2$ [If *m* and *T* are constant]

(i) $PV = P\left(\frac{m}{\rho}\right)$ = constant [As volume $= \frac{m}{\rho}$]

$\therefore \frac{P}{\rho} = \text{constant}$ or $\frac{P_1}{\rho_1} = \frac{P_2}{\rho_2}$ [As *m* = constant]

(ii) $PV = P\left(\frac{N}{n}\right) = \text{constant}$ [As number of molecules per unit volume $n = \frac{N}{V}$ $\therefore$ $V = \frac{N}{n}$]

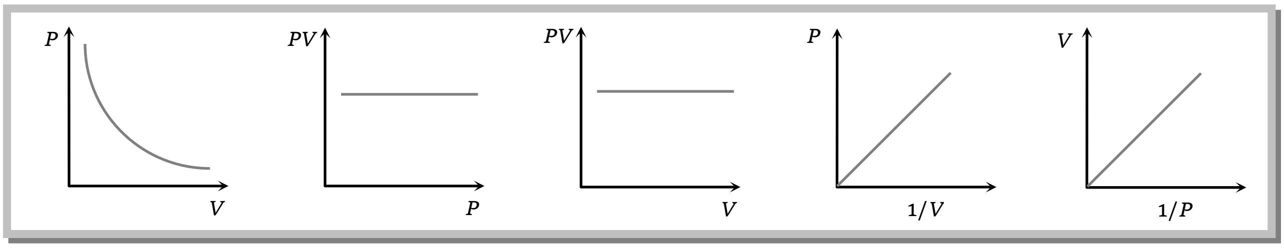
$\therefore \frac{P}{n} = \text{constant}$ or $\frac{P_1}{n_1} = \frac{P_2}{n_2}$ [As *N* = constant]

(iii) According to kinetic theory of gases $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$

$\therefore \quad P \propto \frac{\text{mass of gas}}{V} \times T$ [As $v_{rms} \propto \sqrt{T}$ and mN = Mass of gas]

If mass and temperature of gas remain constant then $P \propto \frac{1}{V}$. This is in accordance with Boyle's law.

(iv) Graphical representation: If *m* and *T* are constant



Sample Problems based on Boyle's law

***Problem* 52.** At constant temperature on increasing the pressure of a gas by 5% will decrease its volume by

(a) 5% (b) 5.26% (c) 4.26% (d) 4.76%

Solution : (d) If $P_1 = P$ then $P_2 = P + 5\%$ of P = 1.05 P

From Boyle's law PV = constant $\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{P}{1.05\,P} = \frac{100}{105}$

Fractional change in volume $= \frac{\Delta V}{V} = \frac{V_2 - V_1}{V_1} = \frac{100 - 105}{105} = -\frac{5}{105}$

$\therefore$ Percentage change in volume $\frac{\Delta V}{V} \times 100\% = -\frac{5}{105} \times 100\% = -4.76\%$ *i.e.* volume decrease by 4.76%.

***Problem* 53.** A cylinder contained 10 *kg* of gas at pressure $10^7\ N/m^2$. The quantity of gas taken out of cylinder if final pressure is $2.5 \times 10^6\ N/m$ is (assume the temperature of gas is constant)

(a) Zero (b) 7.5 *kg* (c) 2.5 *kg* (d) 5 *kg*

Solution : (b) At constant temperature for the given volume of gas $\frac{P_1}{P_2} = \frac{m_1}{m_2}$

$\therefore \frac{10^7}{2.5 \times 10^6} = \frac{10}{m_2} \quad \Rightarrow m_2 = \frac{2.5 \times 10^6 \times 10}{10^7} = 2.5\,kg$

$\therefore$ The quantity of gas taken out of the cylinder = 10 – 2.5 = 7.5 *kg*.

***Problem* 54.** If a given mass of gas occupies a volume of 10 *cc* at 1 atmospheric pressure and temperature of 100°*C* (373.15 *K*). What will be its volume at 4 atmospheric pressure; the temperature being the same

(a) 100 *cc* (b) 400 *cc* (c) 2.5 *cc* (d) 104 *cc*

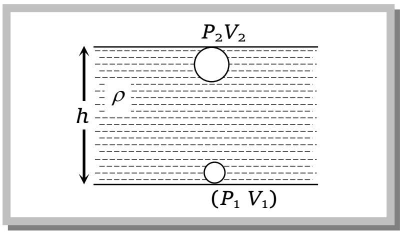
Solution : (c) $P \propto \frac{1}{V} \therefore \frac{V_2}{V_1} = \frac{P_1}{P_2} \Rightarrow V_2 = 10 \times \left(\frac{1}{4}\right) = 2.5\,cc$

Problem **55.** An air bubble of volume V_0 is released by a fish at a depth h in a lake. The bubble rises to the surface. Assume constant temperature and standard atmospheric pressure P above the lake. The volume of the bubble just before touching the surface will be (density of water is ρ)

(a) V_0 (b) $V_0(\rho gh/P)$ (c) $\dfrac{V_0}{\left(1+\dfrac{\rho gh}{P}\right)}$ (d) $V_0\left(1+\dfrac{\rho gh}{P}\right)$

Solution : (d) According to Boyle's law multiplication of pressure and volume will remains constant at the bottom and top.

If P is the atmospheric pressure at the top of the lake and the volume of bubble is V then from $P_1V_1 = P_2V_2$



$$(P+h\rho g)V_0 = PV \Rightarrow V = \left(\frac{P+h\rho g}{P}\right)V_0$$

$$\therefore \quad V = V_0\left[1+\frac{\rho gh}{P}\right]$$

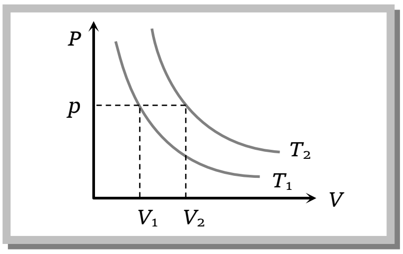
Problem **56.** The adjoining figure shows graph of pressure and volume of a gas at two temperatures T_1 and T_2. Which of the following interferences is correct

(a) $T_1 > T_2$

(b) $T_1 = T_2$

(c) $T_1 < T_2$

(d) No interference can be drawn



Solution : (c) For a given pressure, volume will be more if temperature is more (Charle's law)

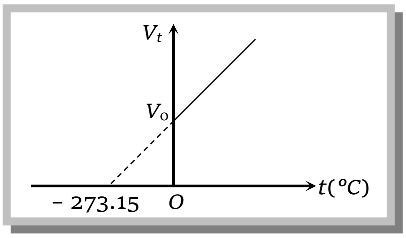
From the graph it is clear that $V_2 > V_1$

$\therefore\ T_2 > T_1$

(2) Charle's law

(i) If the pressure remains constant, the volume of the given mass of a gas increases or decreases by $\dfrac{1}{273.15}$ of its volume at 0°C for each 1°C rise or fall in temperature.

$V_t = V_0\left(1+\dfrac{1}{273.15}t\right)$. This is Charle's law for centigrade scale.



(ii) If the pressure remaining constant, the volume of the given mass of a gas is directly proportional to its absolute temperature.

$V \propto T$ or $\dfrac{V}{T} = \text{constant}$ or $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$ [If m and P are constant]

(iii) $\dfrac{V}{T} = \dfrac{m}{\rho T} = \text{constant}$ [As volume $V = \dfrac{m}{\rho}$]

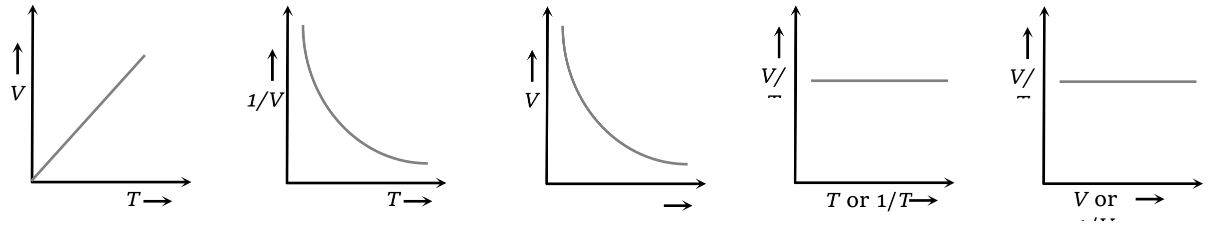
Or $\rho T = \text{constant}$ or $\rho_1 T_1 = \rho_2 T_2$ [As m = constant]

(iv) According to kinetic theory of gases $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$

or $P \propto \frac{\text{Mass of gas}}{V}T$

If mass and pressure of the gas remains constant then $V \propto T$. This is in accordance with Charles law.

(v) Graphical representation: If m and P are constant



[All temperature T are in kelvin]

Sample problems based on Charle's law

***Problem* 57.** A perfect gas at 27°C is heated at constant pressure to 327°C. If original volume of gas at 27°C is V then volume at 327°C is

(a) V (b) $3V$ (c) $2V$ (d) $V/2$

Solution : (c) From Charle's law $V \propto T$ $\therefore \frac{V_2}{V_1} = \frac{T_2}{T_1} = \frac{327+273}{27+273} = \frac{600}{300} = 2 \Rightarrow V_2 = 2V.$

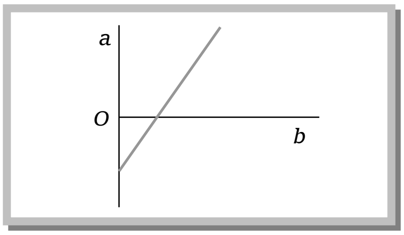
***Problem* 58.** Hydrogen gas is filled in a balloon at 20°C. If temperature is made 40°C, pressure remaining same, what fraction of hydrogen will come out

(a) 0.07 (b) 0.25 (c) 0.5 (d) 0.75

Solution : (a) As $V \propto T$ $\therefore \frac{V_2}{V_1} = \frac{T_2}{T_1} \Rightarrow V_2 = \left(\frac{313}{293}\right)V_1$

Fraction of gas comes out $= \frac{V_2 - V_1}{V_1} = \frac{\left(\frac{313}{293}\right)V_1 - V_1}{V_1} = \frac{20}{293} = 0.07$.

***Problem* 59.** The expansion of unit mass of a perfect gas at constant pressure is shown in the diagram. Here



(a) a = volume, b = °C temperature

(b) a = volume, b = K temperature

(c) a = °C temperature, b = volume

(d) a = K temperature, b = volume

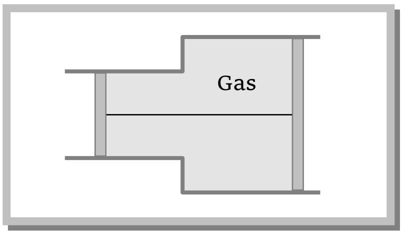
Solution : (c) In the given graph line have a positive slop with X-axis and negative intercept on Y-axis. So we can write the equation of line $y = mx - c$ ...... (i)

According to Charle's law $V_t = \frac{V_0}{273}t + V_0$, by rewriting this equation we get

$$t = \left(\frac{273}{V_0}\right)V_t - 273 \qquad ......(ii)$$

By comparing (i) and (ii) we can say that time is represented on Y-axis and volume in X-axis.

Problem **60.** A gas is filled in the cylinder shown in the figure. The two pistons are joined by a string. If the gas is heated, the pistons will



(a) Move towards left

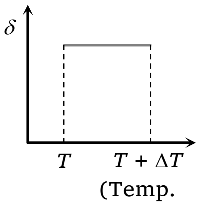
(b) Move towards right

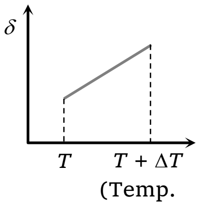
(c) Remain stationary

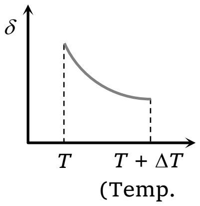
(d) None of these

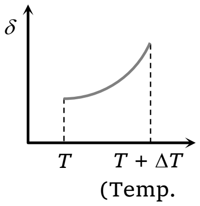
Solution : (b) When temperature of gas increases it expands. As the cross-sectional area of right piston is more, therefore greater force will work on it (because $F = PA$). So piston will move towards right.

Problem **61.** An ideal gas is initially at a temperature T and volume V. Its volume is increased by ΔV due to an increase in temperature ΔT, pressure remaining constant. The quantity $\delta = \frac{\Delta V}{V\Delta T}$ varies with temperature as

(a)


(b)


(c)


(d)


Solution : (c) From ideal gas equation $PV = RT$ .....(i)

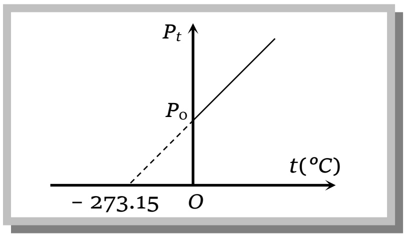
or $P\Delta V = R\Delta T$ .....(ii)

Dividing equation (ii) by (i) we get $\frac{\Delta V}{V} = \frac{\Delta T}{T} \Rightarrow \frac{\Delta V}{V\Delta T} = \frac{1}{T} = \delta$ (given)

$\therefore\ \delta = \frac{1}{T}$. So the graph between δ and T will be rectangular hyperbola.

(3) Gay-Lussac's law or pressure law

(i) The volume remaining constant, the pressure of a given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its pressure at 0°*C* for each 1°*C* rise or fall in temperature.



$$P_t = P_0\left[1 + \frac{1}{273.15}t\right]$$

This is pressure law for centigrade scale.

(ii) The volume remaining constant, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

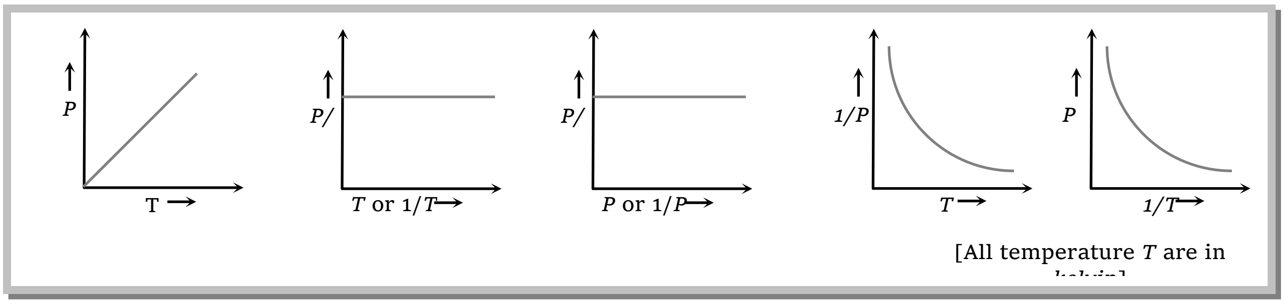
$P \propto T$ or $\frac{P}{T} = \text{constant}$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ [If m and V are constant]

(iii) According to kinetic theory of gases $P=\frac{1}{3}\frac{mN}{V}v_{rms}^2$ [As $v_{rms}^2 \propto T$]

or $P \propto \frac{\text{mass of gas}}{V}T$

If mass and volume of gas remains constant then $P \propto T$. This is in accordance with Gay Lussac’s law.

(4) **Graphical representation :** If *m* and *V* are constants



[All temperature *T* are in

Sample problems based on Gay Lussac's law

***Problem* 62.** On 0°*C* pressure measured by barometer is 760 *mm*. What will be pressure on 100°*C*

(a) 760 *mm* (b) 730 *mm* (c) 780 *mm* (d) None of these

Solution : (d) From Gay Lussac’s law $\frac{P_2}{P_1}=\frac{T_2}{T_1}=\left(\frac{100+273}{0+273}\right)=\frac{373}{273} \Rightarrow P_2=\left(\frac{373}{273}\right)\times 760=1038\ mm$.

***Problem* 63.** If pressure of a gas contained in a closed vessel is increased by 0.4% when heated by 1°*C*, the initial temperature must be

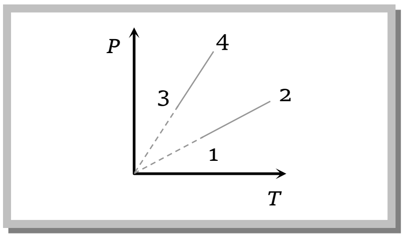
(a) 250 *K* (b) 250°*C* (c) 2500 *K* (d) 25°*C*

Solution : (a) $P_1=P$, $T_1=T$, $P_2=P+$ (0.4% of P) $=P+\frac{0.4}{100}P=P+\frac{P}{250}$ $T_2=T+1$

From Gay Lussac's law $\frac{P_1}{P_2}=\frac{T_1}{T_2} \Rightarrow \frac{P}{P+\frac{P}{250}}=\frac{T}{T+1}$ [As *V* = constant for closed vessel]

By solving we get *T* = 250 *K*.

***Problem* 64.** Pressure versus temperature graph of an ideal gas of equal number of moles of different volumes are plotted as shown in figure. Choose the correct alternative



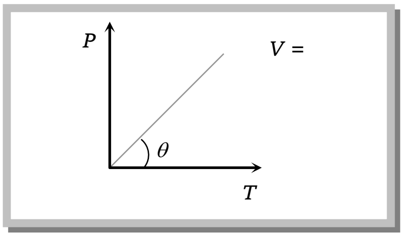
(a) $V_1=V_2, V_3=V_4$ and $V_2>V_3$

(b) $V_1=V_2, V_3=V_4$ and $V_2<V_3$

(c) $V_1=V_2=V_3=V_4$

(d) $V_4>V_3>V_2>V_1$

Solution : (a) From ideal gas equation $PV=\mu RT$ $\therefore$ $P=\frac{\mu R}{V}T$



Comparing this equation with $y=mx$

Slope of line $\tan\theta=m=\frac{\mu R}{V}$ *i.e.* $V \propto \frac{1}{\tan\theta}$

It means line of smaller slope represent greater volume of gas.

For the given problem figure

Point 1 and 2 are on the same line so they will represent same volume *i.e.* $V_1 = V_2$

Similarly point 3 and 4 are on the same line so they will represent same volume *i.e.* $V_3 = V_4$

But $V_1 > V_3$ $(= V_4)$ or $V_2 > V_3$ $(= V_4)$ as slope of line 1-2 is less than 3-4.

(5) **Avogadro's law:** Equal volume of all the gases under similar conditions of temperature and pressure contain equal number of molecules.

According to kinetic theory of gases $PV = \frac{1}{3} m\, N\, v_{rms}^2$

For first gas, $PV = \frac{1}{3} m_1 N_1\, v_{rms(1)}^2$ .....(i)

For second gas, $PV = \frac{1}{3} m_2 N_2\, v_{rms(2)}^2$ .....(ii)

From (i) and (ii) $m_1 N_1\, v_{rms1}^2 = m_2 N_2\, v_{rms2}^2$ .....(iii)

As the two gases are at the same temperature $\frac{1}{2} m_1\, v_{rms1}^2 = \frac{1}{2} m_2\, v_{rms2}^2 = \frac{3}{2} kT \Rightarrow m_1\, v_{rms1}^2 = m_2\, v_{rms2}^2$ .....(iv)

So from equation (iii) we can say that $N_1 = N_2$. This is Avogadro's law.

(i) **Avogadro's number (N_A) :** The number of molecules present in 1 *gm mole* of a gas is defined as Avogadro number.

$N_A = 6.023 \times 10^{23}$ per *gm mole* $= 6.023 \times 10^{26}$ per *kg mole*.

(ii) At S.T.P. or N.T.P. (T = 273 K and P = 1 *atm*) 22.4 *litre* of each gas has 6.023×10^{23} molecule.

(iii) One mole of any gas at S.T.P. occupy 22.4 *litre* of volume

Example : 32 *gm* oxygen, 28 *gm* nitrogen and 2*gm* hydrogen occupy the same volume at S.T.P.

(iv) For any gas 1 *mole* = *M gram* = 22.4 *litre* = 6.023×10^{23} molecule.

Sample problems based on Avogadro's Law

Problem **65.** Temperature of an ideal gas is T K and average kinetic energy is $E = 2.07 \times 10^{-23} T$ *Joule/molecule*. Number of molecules in 1 *litre* gas at S.T.P. will be

(a) 2.68×10^{22} (b) 2.68×10^{25} (c) 2.68×10^{28} (d) 1.68×10^{22}

Solution : (a) As we know that at S.T.P. 22.4 *litre* of gas contains 6.023×10^{23} molecules

$\therefore$ 1 *litre* of gas contain $\frac{6.023 \times 10^{23}}{22.4} = 2.68 \times 10^{22}$ molecules.

Problem **66.** The average kinetic energy per molecule of helium gas at temperature T is E and the molar gas constant is R, then Avogadro's number is

(a) $\frac{RT}{2E}$ (b) $\frac{3RT}{E}$ (c) $\frac{E}{2RT}$ (d) $\frac{3RT}{2E}$

Solution : (d) Average kinetic energy per unit molecule $E=\frac{3}{2}kT \therefore k=\frac{2E}{3T}$

But Avagadro number $=N_A=\frac{R}{k}=\frac{R}{(2E/3T)} \therefore N_A=\frac{3RT}{2E}$.

Problem **67.** One mole of a gas filled in a container at N.T.P., the number of molecules in 1 cm^3 of volume will be

(a) $6.02\times10^{23}/22400$ (b) 6.02×10^{23} (c) 1/22400 (d) $6.02\times10^{23}/76$

Solution : (a) Number of molecule in 22.4 *litre* gas at N.T.P. $=6.023\times10^{23}$

or number of molecule in $22.4\times10^3\ cm^3=6.023\times10^{23}$ [As 22.4 *litre* $=22.4\times10^3\ cm^3$]

$\therefore$ Number of molecules in $1\,cm^3=\frac{6.023\times10^{23}}{22400}$.

(6) **Grahm's law of diffusion:** When two gases at the same pressure and temperature are allowed to diffuse into each other, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas.

We know $v_{rms}=\sqrt{\frac{3P}{\rho}}$ or $v_{rms}\propto\frac{1}{\sqrt{\rho}}$

and rate of diffusion of a gas is proportional to its *rms* velocity *i.e.*, $r\propto v_{rms}$

$\therefore\ r\propto\frac{1}{\sqrt{\rho}}$ or $\frac{r_1}{r_2}=\sqrt{\frac{\rho_2}{\rho_1}}$

(7) **Dalton's law of partial pressure:** The total pressure exerted by a mixture of non-reacting gases occupying a vessel is equal to the sum of the individual pressures which each gases exert if it alone occupied the same volume at a given temperature.

For *n* gases $P=P_1+P_2+P_3+.....P_n$

where *P* = Pressure exerted by mixture and $P_1,P_2,P_3,......P_n=$Partial pressure of component gases.

Sample problems based on Dalton's law

Problem **68.** The capacity of a vessel is 3 *litres*. It contains 6 *gm* oxygen, 8 *gm* nitrogen and 5 *gm* CO_2 mixture at 27°*C*. If *R* = 8.31 *J/mole* × *kelvin*, then the pressure in the vessel in N/m^2 will be (approx.)

(a) 5×10^5 (b) 5×10^4 (c) 10^6 (d) 10^5

Solution : (a) Dalton's law $P=P_1+P_2+P_3=\frac{\mu_1RT}{V}+\frac{\mu_2RT}{V}+\frac{\mu_3RT}{V}=\frac{RT}{V}[\mu_1+\mu_2+\mu_3]=\frac{RT}{V}\left[\frac{m_1}{M_1}+\frac{m_2}{M_2}+\frac{m_3}{M_3}\right]$

$$=\frac{8.31\times300}{3\times10^{-3}}\left[\frac{6}{32}+\frac{8}{28}+\frac{5}{44}\right]=498\times10^3\cong500\times10^3\cong5\times10^5\ N/m^2 .$$

Problem **69.** Two gases occupy two containers *A* and *B* the gas in *A*, of volume $0.10\,m^3$, exerts a pressure of 1.40 *MPa* and that in *B* of volume $0.15\,m^3$ exerts a pressure 0.7 *MPa*. The two containers are united by a tube of negligible volume and the gases are allowed to intermingle. Then it the temperature remains constant, the final pressure in the container will be (in *MPa*)

(a) 0.70 (b) 0.98 (c) 1.40 (d) 2.10

Solution : (b) As the quantity of gas remains constant $\mu_A + \mu_B = \mu$

$$\frac{P_A V_A}{RT} + \frac{P_B V_B}{RT} = \frac{P(V_A + V_B)}{RT} \Rightarrow P = \frac{P_A V_A + P_B V_B}{V_A + V_B} = \frac{1.4 \times 0.1 + 0.7 \times 0.15}{0.1 + 0.15} \Rightarrow P = 0.98\,MPa\,.$$

Problem **70.** The temperature, pressure and volume of two gases *X* and *Y* are *T*, *P* and *V* respectively. When the gases are mixed then the volume and temperature of mixture become *V* and *T* respectively. The pressure and mass of the mixture will be

(a) 2*P* and 2*M* (b) *P* and *M* (c) *P* and 2*M* (d) 2*P* and *M*

Solution : (a) From Dalton's law, Pressure of mixture $= P_1 + P_2 = P + P = 2P$

Similarly mass also will become double *i.e.* 2*M*.

Problem **71.** A closed vessel contains 8*g* of oxygen and 7*g* of nitrogen. The total pressure is 10 *atm* at a given temperature. If now oxygen is absorbed by introducing a suitable absorbent the pressure of the remaining gas in *atm* will be

(a) 2 (b) 10 (c) 4 (d) 5

Solution : (d) From Dalton's law final pressure of the mixture of nitrogen and oxygen

$$P = P_1 + P_2 = \frac{\mu_1 RT}{V} + \frac{\mu_2 RT}{V} = \frac{m_1}{M_1}\frac{RT}{V} + \frac{m_2}{M_2}\frac{RT}{V} = \frac{8}{32}\frac{RT}{V} + \frac{7}{28}\frac{RT}{V} = \frac{RT}{2V} \Rightarrow 10 = \frac{RT}{2V} \qquad .....(i)$$

When oxygen is absorbed then for nitrogen let pressure is $P = \frac{7}{28}\frac{RT}{V}$

$$\Rightarrow \quad P = \frac{RT}{4V} \qquad .....(ii)$$

From equation (i) and (ii) we get pressure of the nitrogen $P = 5\,atm$.

(8) **Ideal gas equation :** From kinetic theory of gases $P = \frac{1}{3}\frac{mN}{V}v_{rms}^2$

$$P \propto \frac{(\text{mass of gas})T}{V} \qquad [\text{As } v_{rms}^2 \propto T\,]$$

If mass of gas is constant then $PV \propto T$ or $PV = RT$. This is ideal gas equation.

Degree of Freedom

The term degree of freedom of a system refers to the possible independent motions, systems can have. or

The total number of independent modes (ways) in which a system can possess energy is called the degree of freedom (f).

The independent motions can be translational, rotational or vibrational or any combination of these.

So the degree of freedom are of three types: (i) Translational degree of freedom

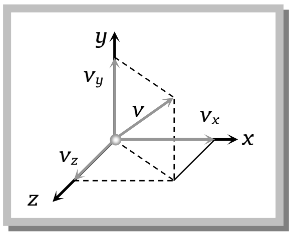
(ii) Rotational degree of freedom

(iii) Vibrational degree of freedom

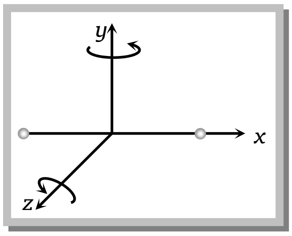
General expression for degree of freedom

$f = 3A - B$; where A = Number of independent particles, B = Number of independent restriction

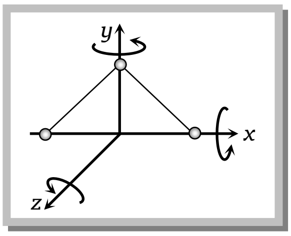
(1) **Monoatomic gas:** Molecule of monoatomic gas can move in any direction in space so it can have three independent motions and hence 3 degrees of freedom (all translational)



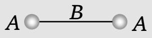
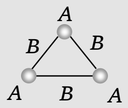
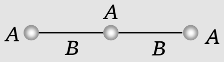
(2) **Diatomic gas:** Molecules of diatomic gas are made up of two atoms joined rigidly to one another through a bond. This cannot only move bodily, but also rotate about one of the three co-ordinate axes. However its moment of inertia about the axis joining the two atoms is negligible compared to that about the other two axes. Hence it can have only two rotational motion. Thus a diatomic molecule has 5 degree of freedom: 3 translational and 2 rotational.



(3) **Triatomic gas (Non-linear):** A non-linear molecule can rotate about any of three co-ordinate axes. Hence it has 6 degrees of freedom: 3 translational and 3 rotational.



(4) Tabular display of degree of freedom of different gases

Atomicity of gas	Example	*A*	*B*	*f* = 3*A* – *B*	Figure
Monoatomic	*He*, *Ne*, *Ar*	1	0	$f = 3$	
Diatomic	H_2, O_2	2	1	$f = 5$	
Triatomic non linear	H_2O	3	3	$f = 6$	
Triatomic linear	CO_2, $BeCl_2$	3	2	$f = 7$	

Note : ☐ The above degrees of freedom are shown at room temperature. Further at high temperature, in case of diatomic or polyatomic molecules, the atoms with in the molecule may also vibrate with respect to each other. In such cases, the molecule will have an additional degrees of freedom, due to vibrational motion.

☐ An object which vibrates in one dimension has two additional degree of freedom. One for the potential energy and one for the kinetic energy of vibration.

☐ A diatomic molecule that is free to vibrate (in addition to translation and rotation) will have 7 (2 + 3 + 2) degrees of freedom.

☐ An atom in a solid though has no degree of freedom for translational and rotational motion, due to vibration along 3 axes has 3 × 2 = 6 degrees of freedom (and not like an ideal gas molecule). When a diatomic or polyatomic gas dissociates into atoms it behaves as monoatomic gas whose degree of freedom are changed accordingly.

Law of Equipartition of Energy

For any system in thermal equilibrium, the total energy is equally distributed among its various degree of freedom. And the energy associated with each molecule of the system per degree of freedom of the system is $\frac{1}{2}kT$.

where $k = 1.38 \times 10^{-23}\ J/K$, T = absolute temperature of the system.

If the system possess degree of freedom *f* then

Total energy associated with each molecule	$\frac{f}{2}kT$
Total energy associated with *N* molecules	$N\frac{f}{2}kT$
Total energy associated with each mole	$\frac{f}{2}RT$
Total energy associated with μ mole	$\frac{\mu f}{2}RT$
Total energy associated with each gram	$\frac{f}{2}rT$
Total energy associated with M_0 gram	$M_0\frac{f}{2}rT$

Sample problems based on Law of equipartition of energy

***Problem* 72.** Energy of all molecules of a monoatomic gas having a volume V and pressure P is $\frac{3}{2}PV$. The total translational kinetic energy of all molecules of a diatomic gas as the same volume and pressure is

(a) $\frac{1}{2}PV$ (b) $\frac{3}{2}PV$ (c) $\frac{5}{2}PV$ (d) 3 PV

Solution : (b) Energy of 1 mole of gas $=\frac{f}{2}RT=\frac{f}{2}PV$ where f = Degree of freedom

Monoatomic or diatomic both gases posses equal degree of freedom for translational motion and that is equal to 3 *i.e.* f = 3 $\therefore\ E=\frac{3}{2}PV$

Although total energy will be different, For monoatomic gas $E_{\text{total}}=\frac{3}{2}PV$ [As f = 3]

For diatomic gas $E_{\text{total}}=\frac{5}{2}PV$ [As f = 5]

***Problem* 73.** The temperature of argon, kept in a vessel is raised by 1°*C* at a constant volume. The total heat supplied to the gas is a combination of translational and rotational energies. Their respective shares are

(a) 60% and 40% (b) 40% and 60% (c) 50% and 50% (d) 100% and 0%

Solution : (d) As argon is a monoatomic gas therefore its molecule will possess only translatory kinetic energy *i.e.* the share of translational and rotational energies will be 100% and 0% respectively.

***Problem* 74.** $CO_2(O-C-O)$ is a triatomic gas. Mean kinetic energy of one gram gas will be (If *N*-Avogadro's number, *k*-Boltzmann's constant and molecular weight of $CO_2=44$)

(a) $3/88\,NkT$ (b) $5/88\,NkT$ (c) $6/88\,NkT$ (d) $7/88\,NkT$

Solution : (d) Mean kinetic energy for μ mole gas $=\mu.\frac{f}{2}RT$

$$\therefore\ E=\mu\frac{7}{2}RT=\left(\frac{m}{M}\right)\frac{7}{2}NkT=\frac{1}{44}\left(\frac{7}{2}\right)NkT=\frac{7}{88}NkT$$

[As f = 7 and M = 44 for CO_2]

***Problem* 75.** At standard temperature and pressure the density of a gas is 1.3 $gm/\ m^3$ and the speed of the sound in gas is 330 *m/sec*. Then the degree of freedom of the gas will be

(a) 3 (b) 4 (c) 5 (d) 6

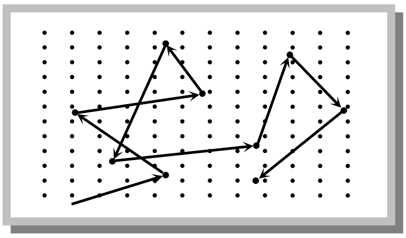
Solution : (c) Given velocity of sound $v_s=330\,\frac{m}{\sec}$, Density of gas $\rho=1.3\frac{kg}{m^3}$, Atomic pressure $P=1.01\times10^5\,\frac{N}{m^2}$

Substituting these value in $v_{\text{sound}}=\sqrt{\frac{\gamma P}{\rho}}$ we get $\gamma=1.41$

Now from $\gamma=1+\frac{2}{f}$ we get $f=\frac{2}{\gamma-1}=\frac{2}{1.4-1}=5.$

Mean Free Path

The molecules of a gas move with high speeds at a given temperature but even then a molecule of the gas takes a very long time to go from one point to another point in the container of the gas. This is due to the fact that a gas molecule suffers a number of collisions with other gas molecules surrounding it. As a result of these collisions, the path followed by a gas molecule in the container of the gas is zig-zag as shown in the figure. During two successive collisions, a molecule of a gas moves in a straight line with constant velocity and the distance travelled by a gas molecule between two successive collisions is known as free path.



The distance travelled by a gas molecule between two successive collisions is not constant and hence the average distance travelled by a molecule during all collisions is to be calculated. This average distance travelled by a gas molecule is known as mean free path.

Let $\lambda_1, \lambda_2, \lambda_3, \dots \lambda_n$ be the distance travelled by a gas molecule during n collisions respectively, then the mean free path of a gas molecule is given by $\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n}{n}$

(1) $\lambda = \frac{1}{\sqrt{2}\pi n d^2}$; where d = Diameter of the molecule, n = Number of molecules per unit volume

(2) As $PV = \mu RT = \mu NkT \Rightarrow \frac{N}{V} = \frac{P}{kT} = n =$ Number of molecule per unit volume

So $\lambda = \frac{1}{\sqrt{2}} \frac{kT}{\pi d^2 P}$

(3) From $\lambda = \frac{1}{\sqrt{2}\pi n d^2} = \frac{m}{\sqrt{2}\pi (mn) d^2} = \frac{m}{\sqrt{2}\pi d^2 \rho}$ [As mn = Mass per unit volume = Density = ρ]

(4) If average speed of molecule is v then

$\lambda = v \times \frac{t}{N} = v \times T$ [As N = Number of collision in time t, T = time interval between two collisions]

Important points

(i) As $\lambda = \frac{m}{\sqrt{2}\pi d^2 \rho}$ $\therefore$ $\lambda \propto \frac{1}{\rho}$ *i.e.* the mean free path is inversely proportional to the density of a gas.

(ii) As $\lambda = \frac{1}{\sqrt{2}} \frac{kT}{\pi d^2 P}$. For constant volume and hence constant number density n of gas molecules, $\frac{P}{T}$ is constant so that λ will not depend on P and T. But if volume of given mass of a gas is allowed to change with P or T then $\lambda \propto T$ at constant pressure and $\lambda \propto \frac{1}{P}$ at constant temperature.

Sample Problems based on Mean free path

Problem 76. If the mean free path of atoms is doubled then the pressure of gas will become

(a) $P/4$ (b) $P/2$ (c) $P/8$ (d) P

Solution : (b) As $\lambda = \frac{1}{\sqrt{2}}\frac{kT}{\pi d^2 P}$ $\therefore P \propto \frac{1}{\lambda}$ *i.e.* by increasing λ two times pressure will become half.

Problem 77. The mean free path of nitrogen molecules at a pressure of 1.0 *atm* and temperature 0°*C* is $0.8\times 10^{-7}\,m$. If the number of density of molecules is $2.7\times 10^{25}\,per\,m^3$, then the molecular diameter is

(a) $3.2\,nm$ (b) $3.2\,\mathring{A}$ (c) $3.2\,\mu m$ (d) $2.3\,mm$

Solution : (b) Mean free path $\lambda = 0.8\times 10^{-7}\,m$ number of molecules per unit volume $n = 2.7\times 10^{25}$ per m^3

Substituting these value in $\lambda = \frac{1}{\sqrt{2}\pi n d^2}$ we get $d = \sqrt{1.04\times 10^{-19}} = 3.2\times 10^{-10}\,m = 3.2\,\mathring{A}$

Specific heat or Specific Heat Capacity

It characterises the nature of the substance in response to the heat supplied to the substance. Specific heat can be defined by two following ways: Gram specific heat and Molar specific heat.

(1) **Gram specific heat:** Gram specific heat of a substance may be defined as the amount of heat required to raise the temperature of unit mass of the substance by unit degree.

Gram specific heat $c = \frac{\Delta Q}{m\Delta T}$

Units : $\frac{cal}{gm\times °C}$, $\frac{cal}{gm\times kelvin}$, $\frac{Joule}{kg\times kelvin}$

Dimension : $[L^2T^{-2}\theta^{-1}]$

(2) **Molar specific heat:** Molar specific heat of a substance may be defined as the amount of heat required to raise the temperature of one gram mole of the substance by a unit degree, it is represented by capital (C)

$$C = \frac{Q}{\mu\Delta T}$$

Units : $\frac{calorie}{mole\times °C}$, $\frac{calorie}{mole\times kelvin}$ or $\frac{Joule}{mole\times kelvin}$

Important points

(1) $C = Mc = \frac{M}{m}\frac{\Delta Q}{\Delta T} = \frac{1}{\mu}\frac{\Delta Q}{\Delta T}$ $\left[\text{As}\,\mu = \frac{m}{M}\right]$

i.e. molar specific heat of the substance is M times the gram specific heat, where M is the molecular weight of that substance.

(2) Specific heat for hydrogen is maximum $c = 3.5 \frac{cal}{gm \times °C}$.

(3) In liquids, water has maximum specific heat $c = 1 \frac{cal}{gm \times °C}$.

(4) Specific heat of a substance also depends on the state of substance *i.e.* solid, liquid or gas.

Example : $c_{\text{ice}} = 0.5 \frac{cal}{gm \times °C}$, $c_{\text{water}} = 1 \frac{cal}{gm \times °C}$, $c_{\text{steam}} = 0.47 \frac{cal}{gm \times °C}$

(5) Specific heat also depends on the conditions of the experiment *i.e.* the way in which heat is supplied to the body. In general, experiments are made either at constant volume or at constant pressure.

In case of solids and liquids, due to small thermal expansion, the difference in measured values of specific heats is very small and is usually neglected. However, in case of gases, specific heat at constant volume is quite different from that at constant pressure.

Specific Heat of Gases

In case of gases, heat energy supplied to a gas is spent not only in raising the temperature of the gas but also in expansion of gas against atmospheric pressure.

Hence specific heat of a gas, which is the amount of heat energy required to raise the temperature of one gram of gas through a unit degree shall not have a single or unique value.

(i) If the gas is compressed suddenly and no heat is supplied from outside *i.e.* $\Delta Q = 0$, but the temperature of the gas raises on the account of compression.

$$\therefore \quad C = \frac{\Delta Q}{m(\Delta T)} = 0 \qquad i.e. \quad C = 0$$

(ii) If the gas is heated and allowed to expand at such a rate that rise in temperature due to heat supplied is exactly equal to fall in temperature due to expansion of the gas.

i.e. $\Delta T = 0$

$$\therefore \quad C = \frac{\Delta Q}{m(\Delta T)} = \frac{\Delta Q}{0} = \infty \qquad i.e. \quad C = \infty$$

(iii) If rate of expansion of the gas were slow, the fall in temperature of the gas due to expansion would be smaller than the rise in temperature of the gas due to heat supplied. Therefore, there will be some net rise in temperature of the gas *i.e.* ΔT will be positive.

$$\therefore \quad C = \frac{\Delta Q}{m(\Delta T)} = \text{positive} \qquad i.e. \quad C = \text{positive}$$

(iv) If the gas were to expand very fast, fall of temperature of gas due to expansion would be greater than rise in temperature due to heat supplied. Therefore, there will be some net fall in temperature of the gas *i.e.* ΔT will be negative.

$$C = \frac{\Delta Q}{m(-\Delta T)} = \text{negative} \qquad i.e. \quad C = \text{negative}$$

Hence the specific heat of gas can have any positive value ranging from zero to infinity. Further it can even be negative. The exact value depends upon the mode of heating the gas. Out of many values of specific heat of a gas, two are of special significance.

(1) **Specific heat of a gas at constant volume (c_v) :** The specific heat of a gas at constant volume is defined as the quantity of heat required to raise the temperature of unit mass of gas through 1 K when its volume is kept constant, *i.e.*, $c_v = \frac{(\Delta Q)_v}{m\Delta T}$

If instead of unit mass, 1 mole of gas is considered, the specific heat is called molar specific heat at constant volume and is represented by capital C_v.

$$C_v = Mc_v = \frac{M(\Delta Q)_v}{m\Delta T} = \frac{1}{\mu}\frac{(\Delta Q)_v}{\Delta T} \qquad \left[\text{As}\,\mu = \frac{m}{M}\right]$$

(2) **Specific heat of a gas at constant pressure (c_p) :** The specific heat of a gas at constant pressure is defined as the quantity of heat required to raise the temperature of unit mass of gas through 1 K when its pressure is kept constant, *i.e.*, $c_P = \frac{(\Delta Q)_P}{m\Delta T}$

If instead of unit mass, 1 mole of gas is considered, the specific heat is called molar specific heat at constant pressure and is represented by C_p.

$$C_p = MC_p = \frac{M(\Delta Q)_P}{m\Delta T} = \frac{1}{\mu}\frac{(\Delta Q)_P}{\Delta T} \qquad \left[\text{As}\,\mu = \frac{m}{M}\right]$$

Mayer's Formula

Out of two principle specific heats of a gas, C_p is more than C_v because in case of C_v, volume of gas is kept constant and heat is required only for raising the temperature of one gram mole of the gas through 1°C or 1 K.

No heat, what so ever, is spent in expansion of the gas.

It means that heat supplied to the gas increases its internal energy only *i.e.*

$$(\Delta Q)_v = \Delta U = \mu C_v \Delta T \qquad \text{.....(i)}$$

while in case of C_p the heat is used in two ways

(i) In increasing the temperature of the gas by ΔT

(ii) In doing work, due to expansion at constant pressure (ΔW)

So $(\Delta Q)_p = \Delta U + \Delta W = \mu C_p \Delta T$ .....(ii)

From equation (i) and (ii) $\mu C_p \Delta T - \mu C_v \Delta T = \Delta W$

$\Rightarrow$ $\mu \Delta T(C_p - C_v) = P\Delta V$ [For constant P, $\Delta W = P\Delta V$]

$\Rightarrow$ $C_p - C_v = \frac{P\Delta V}{\mu \Delta T}$ [From $PV = \mu RT$, At constant pressure $P\Delta V = \mu R\Delta T$]

$\Rightarrow$ $C_p - C_v = R$

This relation is called Mayer's formula and shows that $C_p > C_v$ *i.e.* molar specific heat at constant pressure is greater than that at constant volume.

Specific Heat in Terms of Degree of Freedom

We know that kinetic energy of one mole of the gas, having f degrees of freedom can be given by

$$E = \frac{f}{2}RT \qquad \text{.....(i)}$$

where T is the temperature of the gas but from the definition of C_v, if dE is a small amount of heat energy required to raise the temperature of 1 *gm* mole of the gas at constant volume, through a temperature dT then

$$dE = \mu C_v dT = C_v\, dT \text{ or } C_v = \frac{dE}{dT} \qquad [\text{As } \mu = 1] \qquad \text{.....(ii)}$$

Putting the value of E from equation (i) we get $C_v = \frac{d}{dT}\left(\frac{f}{2}RT\right) = \frac{f}{2}R$

$$\therefore \qquad C_v = \frac{f}{2}R$$

From the Mayer's formula $C_p - C_v = R \Rightarrow C_p = C_v + R = \frac{f}{2}R + R = \left(\frac{f}{2}+1\right)R$

$$\therefore \qquad C_p = \left(\frac{f}{2}+1\right)R$$

Ratio of C_p and C_v : $\gamma = \frac{C_p}{C_v} = \frac{\left(\frac{f}{2}+1\right)R}{\frac{f}{2}R} = 1 + \frac{2}{f}$

$$\therefore \qquad \gamma = 1 + \frac{2}{f}$$

Important points

(i) Value of γ is always more than 1. So we can say that always $C_p > C_v$.

(ii) Value of γ is different for monoatomic, diatomic and triatomic gases.

(iii) As $\gamma = 1 + \frac{2}{f} \quad \Rightarrow \frac{2}{f} = \gamma - 1 \Rightarrow \frac{f}{2} = \frac{1}{\gamma - 1}$

$$\therefore\ C_v = \frac{f}{2}R = \frac{R}{\gamma - 1}$$

and $C_p = \left(\frac{f}{2}+1\right)R = \left(\frac{1}{\gamma-1}+1\right)R = \left(\frac{\gamma}{\gamma-1}\right)R$

Specific heat and kinetic energy for different gases

		Monoatomic	**Diatomic**	**Triatomic non-linear**	**Triatomic linear**
Atomicity	A	1	2	3	3
Restriction	B	0	1	3	2
Degree of freedom	$f = 3A - B$	3	5	6	7
Molar specific heat at constant volume	$C_v = \frac{f}{2}R = \frac{R}{\gamma - 1}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$	$\frac{7}{2}R$
Molar specific heat at constant pressure	$C_p = \left(\frac{f}{2} + 1\right)R = \left(\frac{\gamma}{\gamma - 1}\right)R$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$	$\frac{9}{2}R$
Ratio of C_p and C_v	$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{f}$	$\frac{5}{3} \simeq 1.66$	$\frac{7}{5} \simeq 1.4$	$\frac{4}{3} \simeq 1.33$	$\frac{9}{7} \simeq 1.28$
Kinetic energy of 1 mole	$E_{\text{mole}} = \frac{f}{2}RT$	$\frac{3}{2}RT$	$\frac{5}{2}RT$	$3RT$	$\frac{7}{2}RT$
Kinetic energy of 1 molecule	$E_{\text{molecule}} = \frac{f}{2}kT$	$\frac{3}{2}kT$	$\frac{5}{2}kT$	$3kT$	$\frac{7}{2}kT$
Kinetic energy of 1 *gm*	$E_{\text{gram}} = \frac{f}{2}rT$	$\frac{3}{2}rT$	$\frac{5}{2}rT$	$3rT$	$\frac{7}{2}rT$

Sample Problems based on Specific heat

***Problem* 78.** Find the ratio of specific heat at constant pressure to the specific heat constant volume for NH_3

(a) 1.33 (b) 1.44 (c) 1.28 (d) 1.67

Solution : (c) For polyatomic gas ratio of specific heat $\gamma < 1.33$

Because we know that as the atomicity of gas increases its value of γ decreases.

***Problem* 79.** For a gas $\frac{R}{C_v} = 0.67$. This gas is made up of molecules which are

(a) Diatomic (b) Mixture of diatomic and polyatomic molecules

(c) Monoatomic (d) Polyatomic

Solution : (c) By comparing with relation $C_v = \frac{R}{\gamma - 1}$ we get $\gamma - 1 = 0.67$ or $\gamma = 1.67$ *i.e.* the gas is monoatomic.

Problem **80.** 40 *calories* of heat is needed to raise the temperature of 1 *mole* of an ideal monoatomic gas from 20°*C* to 30°*C* at a constant pressure. The amount of heat required to raise its temperature over the same interval at a constant volume $(R = 2\,calorie\,mole^{-1}K^{-1})$ is

(a) 20 *calorie* (b) 40 *calorie* (c) 60 *calorie* (d) 80 *calorie*

Solution : (a) At constant pressure $(\Delta Q)_p = \mu C_p \Delta T = 1 \times C_p \times (30 - 20) = 40 \Rightarrow C_p = 4\frac{calorie}{mole\ kelvin}$

$\therefore\ C_v = C_p - R = 4 - 2 = 2\frac{calorie}{mole \times kelvin}$

Now $(\Delta Q)_v = \mu C_v \Delta T = 1 \times 2 \times (30 - 20) = 20\ calorie$

Problem **81.** At constant volume the specific heat of a gas is $\frac{3R}{2}$, then the value of γ will be

(a) $\frac{3}{2}$ (b) $\frac{5}{2}$ (c) $\frac{5}{3}$ (d) None of the above

Solution : (c) Specific heat at constant volume $C_v = \frac{R}{\gamma - 1} = \frac{3R}{2}$ (given)

$\therefore\quad \gamma - 1 = \frac{2}{3} \quad \Rightarrow \quad \gamma = \frac{5}{3}$.

Problem **82.** For a gas the difference between the two specific heats is 4150 *J/kg K*. What is the specific heats at constant volume of gas if the ratio of specific heat is 1.4

(a) 8475 *J/kg - K* (b) 5186 *J/kg - K* (c) 1660 *J/kg - K* (d) 10375 *J/kg - K*

Solution : (d) Given $c_p - c_v = 4150$ .....(i) and $\frac{c_p}{c_v} = 1.4 \Rightarrow c_p = 1.4c_v$ .....(ii)

By substituting the value of c_p in equation (i) we get $1.4c_v - c_v = 4150 \Rightarrow 0.4c_v = 4150$

$\therefore\quad c_v = \frac{4150}{0.4} = 10375\ J/kg\text{-}K$.

Problem **83.** Two cylinders *A* and *B* fitted with pistons contain equal amounts of an ideal diatomic gas at 300*K*. The piston of *A* is free to move while that of *B* is held fixed. The same amount of heat is given to the gas in each cylinder. If the rise in temperature of the gas in *A* is 30 *K*, then the rise in temperature of the gas in *B* is

(a) 30 *K* (b) 18 *K* (c) 50 *K* (d) 42 *K*

Solution : (d) In both cylinders *A* and *B* the gases are diatomic (γ = 1.4). Piston *A* is free to move *i.e.* it is isobaric process. Piston *B* is fixed *i.e.* it is isochoric process. If same amount of heat ΔQ is given to both then

$$(\Delta Q)_{\text{isobaric}} = (\Delta Q)_{\text{isochoric}}$$

$$\mu C_p (\Delta T)_A = \mu C_v (\Delta T)_B \quad \Rightarrow (\Delta T)_B = \frac{C_p}{C_v}(\Delta T)_A = \gamma(\Delta T)_A = 1.4 \times 30 = 42\ K.$$

Problem **84.** The specific heat of a gas

(a) Has only two values of C_p and C_v (b) Has a unique value at a given temperature

(c) Can have any value between 0 and ∞ (d) Depends upon the mass of the gas

Solution : (c) Range of specific heat varies from positive to negative and from zero to infinite. It depends upon the nature of process.

Problem 85. The specific heat at constant volume for the monoatomic argon is 0.075 *kcal/kg-K* whereas its gram molecular specific heat $C_v = 2.98$ *cal/mole/K*. The mass of the argon atom is (Avogadro's number $= 6.02 \times 10^{23}$ *molecules/mole*)

(a) $6.60 \times 10^{-23}\ gm$ (b) $3.30 \times 10^{-23}\ gm$ (c) $2.20 \times 10^{-23}\ gm$ (d) $13.20 \times 10^{-23}\ gm$

Solution : (a) Molar specific heat = Molecular weight × Gram specific heat

$$C_v = M \times c_v$$

$$\Rightarrow \quad 2.98 \frac{calorie}{mole \times kelvin} = M \times 0.075 \frac{kcal}{kg\text{ - }kelvin} = M \times \frac{0.075 \times 10^3}{10^3} \frac{calorie}{gm \times kelvin}$$

$\therefore$ molecular weight of argon $M = \dfrac{2.98}{0.075} = 39.7\ gm$

i.e. mass of 6.023×10^{23} atom = 39.7 *gm* $\therefore$ mass of single atom

$$= \frac{39.7}{6.023 \times 10^{23}} = 6.60 \times 10^{-23}\ gm.$$

Problem 86. When an ideal diatomic gas is heated at constant pressure, the fraction of the heat energy supplied which increases the internal energy of the gas is

(a) 2/5 (b) 3/5 (c) 3/7 (d) 5/7

Solution : (d) When a gas is heated at constant pressure then its one part goes to increase the internal energy and another part for work done against external pressure *i.e.* $(\Delta Q)_p = \Delta U + \Delta W$

$$\Rightarrow \mu C_p \Delta T = \mu C_v \Delta T + P\Delta V$$

So fraction of energy that goes to increase the internal energy $\dfrac{\Delta U}{(\Delta Q)_p} = \dfrac{C_v}{C_p} = \dfrac{1}{\gamma} = \dfrac{5}{7}$ [As $\gamma = \dfrac{7}{5}$ for diatomic gas]

Problem 87. The temperature of 5 mole of a gas which was held at constant volume was changed from 100°*C* to 120°*C*. The change in internal energy was found to be 80 *J*. The total heat capacity of the gas at constant volume will be equal to

(a) $8\ J\,K^{-1}$ (b) $0.8\ J\,K^{-1}$ (c) $4\ J\,K^{-1}$ (d) $0.4\ J\,K^{-1}$

Solution : (c) At constant volume total energy will be utilised in increasing the temperature of gas

i.e. $(\Delta Q)_v = \mu C_v \Delta T = \mu C_v (120 - 100) = 80$

$\Rightarrow \quad \mu C_v = \dfrac{80}{20} = 4$ *Joule/kelvin*. This is the heat capacity of 5 *mole* gas.

Problem 88. A gas, is heated at constant pressure. The fraction of heat supplied used for external work is

(a) $\dfrac{1}{\gamma}$ (b) $\left(1 - \dfrac{1}{\gamma}\right)$ (c) $\gamma - 1$ (d) $\left(1 - \dfrac{1}{\gamma^2}\right)$

Solution : (b) We know fraction of given energy that goes to increase the internal energy $= \dfrac{1}{\gamma}$

So we can say the fraction of given energy that supplied for external work $= 1 - \dfrac{1}{\gamma}$.

***Problem* 89.** A monoatomic gas expands at constant pressure on heating. The percentage of heat supplied that increases the internal energy of the gas and that is involved in the expansion is

(a) 75%, 25% (b) 25%, 75% (c) 60%, 40% (d) 40%, 60%

Solution : (c) Fraction of energy supplied for increment in internal energy $=\frac{1}{\gamma}=\frac{3}{5}$

$\left[\text{As } \gamma=\frac{5}{3} \text{ for monoatomic gas}\right]$

$\therefore$ Percentage energy $=\frac{30}{5}=60\%$

Fraction of energy supplied for external work done $=1-\frac{1}{\gamma}=\frac{\gamma-1}{\gamma}=\frac{\frac{5}{3}-1}{\frac{5}{3}}=\frac{2}{5}$

$\therefore$ Percentage energy $=\frac{2}{5}\times 100\%=40\%$.

***Problem* 90.** The average degrees of freedom per molecule for a gas is 6. The gas performs 25 *J* of work when it expands at constant pressure. The heat absorbed by gas is

(a) 75 *J* (b) 100 *J* (c) 150 *J* (d) 125 *J*

Solution : (b) As f = 6 (given) $\therefore\ \gamma=1+\frac{2}{f}=1+\frac{2}{6}=\frac{4}{3}$

Fraction of energy given for external work $\frac{\Delta W}{\Delta Q}=\left(1-\frac{1}{\gamma}\right)$

$$\Rightarrow \frac{25}{\Delta Q}=\left(1-\frac{1}{4/3}\right)=1-\frac{3}{4}=\frac{1}{4} \Rightarrow \Delta Q=25\times 4=100\ Joule$$

***Problem* 91.** Certain amount of an ideal gas are contained in a closed vessel. The vessel is moving with a constant velocity *v*. The molecular mass of gas is *M*. The rise in temperature of the gas when the vessel is suddenly stopped is $(\gamma=C_P/C_V)$

(a) $\frac{Mv^2}{2R(\gamma+1)}$ (b) $\frac{Mv^2(\gamma-1)}{2R}$ (c) $\frac{Mv^2}{2R(\gamma+1)}$ (d) $\frac{Mv^2}{2R(\gamma+1)}$

Solution : (b) If *m* is the total mass of the gas then its kinetic energy $=\frac{1}{2}mv^2$

When the vessel is suddenly stopped then total kinetic energy will increase the temperature of the gas (because process will be adiabatic) *i.e.* $\frac{1}{2}mv^2=\mu C_v\Delta T=\frac{m}{M}C_v\Delta T$

[As $C_v=\frac{R}{\gamma-1}$]

$$\Rightarrow \frac{m}{M}\frac{R}{\gamma-1}\Delta T=\frac{1}{2}mv^2 \Rightarrow \Delta T=\frac{Mv^2(\gamma-1)}{2R}.$$

***Problem* 92.** The density of a polyatomic gas is standard conditions is 0.795 kgm^{-3}. The specific heat of the gas at constant volume is

(a) $930\ J\text{-}kg^{-1}K^{-1}$ (b) $1400\ J\text{-}kg^{-1}K^{-1}$ (c) $1120\ J\text{-}kg^{-1}K^{-1}$ (d) $925\ J\text{-}kg^{-1}K^{-1}$

Solution : (b) Ideal gas equation for *m gram* gas $PV = mrT$ [where *r* = Specific gas constant]

or $P = \frac{m}{V}rT = \rho rT \Rightarrow r = \frac{P}{\rho T} = \frac{1.013 \times 10^5}{0.795 \times 273} = 466.7$

Specific heat at constant volume $c_v = \frac{r}{\gamma - 1} = \frac{466.7}{\frac{4}{3} - 1} = 1400 \frac{J}{kg.kelvin}$

$\left[\gamma = \frac{4}{3} \text{ for polyatomic gas}\right]$

***Problem* 93.** The value of $C_p - C_v = 1.00\,R$ for a gas in state *A* and $C_p - C_v = 1.06R$ in another state. If P_A and P_B denote the pressure and T_A and T_B denote the temperatures in the two states, then

(a) $P_A = P_B$, $T_A > T_B$ (b) $P_A > P_B$, $T_A = T_B$ (c) $P_A < P_B$, $T_A > T_B$ (d) $P_A > P_B$, $T_A < T_B$

Solution : (c) For state *A*, $C_p - C_v = R$ *i.e.* the gas behaves as ideal gas.

For state *B*, $C_p - C_v = 1.06\,R (\neq R)$ *i.e.* the gas does not behave like ideal gas.

and we know that at high temperature and at low pressure nature of gas may be ideal.

So we can say that $P_A < P_B$ and $T_A > T_B$

Gaseous Mixture

If two non-reactive gases are enclosed in a vessel of volume *V*. In the mixture μ_1 moles of one gas are mixed with μ_2 moles of another gas. If N_A is Avogadro's number then

Number of molecules of first gas $N_1 = \mu_1 N_A$ and number of molecules of second gas $N_2 = \mu_2 N_A$

(i) Total mole fraction $\mu = (\mu_1 + \mu_2)$.

(ii) If M_1 is the molecular weight of first gas and M_2 that of second gas.

Then molecular weight of mixture will be $M = \frac{\mu_1 M_1 + \mu_2 M_2}{\mu_1 + \mu_2}$

(iii) Specific heat of the mixture at constant volume will be

$$C_{V_{mix}} = \frac{\mu_1 C_{V_1} + \mu_2 C_{V_2}}{\mu_1 + \mu_2} = \frac{\mu_1\left(\frac{R}{\gamma_1 - 1}\right) + \mu_2\left(\frac{R}{\gamma_2 - 1}\right)}{\mu_1 + \mu_2} = \frac{R}{\mu_1 + \mu_2}\left[\frac{\mu_1}{\gamma_1 - 1} + \frac{\mu_2}{\gamma_2 - 1}\right]$$

$$\therefore \quad C_{V_{mix}} = \frac{R}{\frac{m_1}{M_1} + \frac{m_2}{M_2}}\left[\frac{m_1/M_1}{\gamma_1 - 1} + \frac{m_2/M_2}{\gamma_2 - 1}\right]$$

(iv) Specific heat of the mixture at constant pressure will be $C_{P_{mix}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2}}{\mu_1 + \mu_2}$

$$\Rightarrow \quad C_{P_{mix}} = \frac{\mu_1\left(\frac{\gamma_1}{\gamma_1 - 1}\right)R + \mu_2\left(\frac{\gamma_2}{\gamma_2 - 1}\right)R}{\mu_1 + \mu_2} = \frac{R}{\mu_1 + \mu_2}\left[\mu_1\left(\frac{\gamma_1}{\gamma_1 - 1}\right) + \mu_2\left(\frac{\gamma_2}{\gamma_2 - 1}\right)\right]$$

$$\therefore \quad C_{P_{mix}} = \frac{R}{\frac{m_1}{M_1} + \frac{m_2}{M_2}}\left[\frac{m_1}{M_1}\left(\frac{\gamma_1}{\gamma_1 - 1}\right) + \frac{m_2}{M_2}\left(\frac{\gamma_2}{\gamma_2 - 1}\right)\right]$$

(v) $$\gamma_{\text{mixture}} = \frac{C_{P_{mix}}}{C_{V_{mix}}} = \frac{\frac{(\mu_1 C_{P_1} + \mu_2 C_{P_2})}{\mu_1 + \mu_2}}{\frac{(\mu_1 C_{V_1} + \mu_2 C_{V_2})}{\mu_1 + \mu_2}} = \frac{\mu_1 C_{P_1} + \mu_2 C_{P_2}}{\mu_1 C_{V_1} + \mu_2 C_{V_2}} = \frac{\left\{\mu_1\left(\frac{\gamma_1}{\gamma_1 - 1}\right)R + \mu_2\left(\frac{\gamma_2}{\gamma_2 - 1}\right)R\right\}}{\left\{\mu_1\left(\frac{R}{\gamma_1 - 1}\right) + \mu_2\left(\frac{R}{\gamma_2 - 1}\right)\right\}}$$

$$\therefore \ \gamma_{\text{mixture}} = \frac{\frac{\mu_1\gamma_1}{\gamma_1 - 1} + \frac{\mu_2\gamma_2}{\gamma_2 - 1}}{\frac{\mu_1}{\gamma_1 - 1} + \frac{\mu_2}{\gamma_2 - 1}} = \frac{\mu_1\gamma_1(\gamma_2 - 1) + \mu_2\gamma_2(\gamma_1 - 1)}{\mu_1(\gamma_2 - 1) + \mu_2(\gamma_1 - 1)}$$

Sample problems based on Mixture

***Problem* 94.** If two moles of diatomic gas and one mole of monoatomic gas are mixed with then the ratio of specific heats is

(a) $\frac{7}{3}$ (b) $\frac{5}{4}$ (c) $\frac{19}{13}$ (d) $\frac{15}{19}$

Solution : (c) $\mu_1 = 1$, $\gamma_1 = \frac{5}{3}$ (for monoatomic gas) and $\mu_2 = 2$, $\gamma_2 = \frac{7}{5}$ (for diatomic gas)

From formula $$\gamma_{\text{mixture}} = \frac{\frac{\mu_1\gamma_1}{\gamma_1 - 1} + \frac{\mu_2\gamma_2}{\gamma_2 - 1}}{\frac{\mu_1}{\gamma_1 - 1} + \frac{\mu_2}{\gamma_2 - 1}} = \frac{\frac{1 \times \frac{5}{3}}{\frac{5}{3} - 1} + \frac{2 \times \frac{7}{5}}{\frac{7}{5} - 1}}{\frac{1}{\frac{5}{3} - 1} + \frac{2}{\frac{7}{5} - 1}} = \frac{5/2 + 7}{3/2 + 5} = \frac{19}{13}$$

***Problem* 95.** 22 *gm* of CO_2 at 27°*C* is mixed with 16 *gm* o*f* O_2 at 37°*C*. The temperature of the mixture is

(a) 32°*C* (b) 27°*C* (c) 37°*C* (d) 30.5°*C*

Solution : (a) Let *t* is the temperature of mixture

Heat gained by CO_2 = Heat lost by O_2

$$\Rightarrow \quad \mu_1 C_{v_1} \Delta T_1 = \mu_2 C_{v_2} \Delta T_2$$

$$\Rightarrow \quad \frac{22}{44}(3R)(t - 27) = \frac{16}{32}\left(\frac{5}{2}R\right)(37 - t)$$

$$\Rightarrow \quad 3(t - 27) = \frac{5}{2}(37 - t)$$

By solving we get $t = 32°C$.

Problem **96.** A gas mixture consists of 2 mole of oxygen and 4 mole of argon at temperature T. Neglecting all vibrational modes, the total internal energy of the system is

(a) 4 RT (b) 15 RT (c) 9 RT (d) 11 RT

Solution : (d) Total internal energy of system $= U_{\text{oxygen}} + U_{\text{argon}} = \mu_1 \frac{f_1}{2} RT + \mu_2 \frac{f_2}{2} RT$

$= 2\frac{5}{2} RT + 4\frac{3}{2} RT = 5\,RT + 6\,RT = 11\,RT$ [As f_1 = 5 (for oxygen) and f_2 = 3 (for argon)]