

Physics : Unit 1 - Kinetic Theory of Gases

Kinetic theory of gases

The kinetic theory of gases is the study that relates the microscopic properties of gas molecules (like speed, momentum, kinetic energies etc.) with the macroscopic properties of gas molecules (like pressure, temperature and volume).

Fundamental postulates of kinetic theory

1. The molecules of a gas are considered to be rigid, perfectly elastic, identical in all respects. They are solid spheres. Their size is negligible compared to intermolecular distances.
2. The molecules are in random motion in all directions with all possible velocities.
3. The molecules collide with each other and with the walls of the container. At each collision, velocity changes but the molecular density is constant in steady state.
4. As the collisions are perfectly elastic, there is no force of attraction or repulsion between the molecules. Thus the energy is only kinetic.
5. Between any two successive collisions, molecules travel with uniform velocity along a straight line.

Expression for Pressure of the gas :

Consider a gas contained in a cubical vessel of side l with perfectly elastic walls containing a large number of molecules.

Let c_1 be the velocity of a molecule in a direction as shown. This can be resolved into three components u_1 , v_1 and w_1 along X, Y and Z directions as shown. Then

$$c_1^2 = u_1^2 + v_1^2 + w_1^2 \quad \dots\dots(1)$$

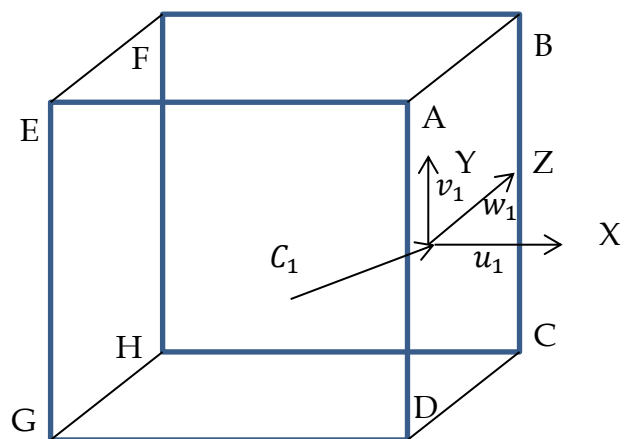
The momentum of this molecule that strikes the wall ABCD of the vessel is equal to mu_1 where m is its mass.

As the collision is elastic, the molecule will rebound with same momentum i.e. mu_1 .

The change in momentum due to impact is equal to $mu_1 - (-mu_1) = 2mu_1$.

It strikes the wall EFHG and returns back to ABCD after travelling a distance $2l$.

The time between the successive collisions (time for one collision) on ABCD is $\frac{2l}{u_1}$.



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Thus the number of collisions per second, this molecule makes with ABCD is $\frac{u_1}{2l}$.

Hence the rate of change of momentum = change in momentum \times number of collisions per second is equal to $2mu_1 \times \frac{u_1}{2l} = \frac{mu_1^2}{l}$.

From Newton's second law, rate of change of momentum = impressed force.

If f_1 is the force, then $f_1 = \frac{mu_1^2}{l}$ along X - direction.

Similarly, the force on another molecule of velocity c_2 whose components are u_2, v_2 and w_2 due to impact is $f_3 = \frac{mu_2^2}{l}$ along X - direction.

Hence the total force F_x on the face ABCD due to impacts of all the n molecules in the X - direction is given by $F_x = \frac{m}{l}(u_1^2 + u_2^2 + u_3^2 \dots \dots \dots + u_n^2)$ (2)

Since pressure is force per unit area, the pressure P_x on ABCD is given by

$$P_x = \frac{F_x}{l^2} = \frac{m}{l^3}(u_1^2 + u_2^2 + u_3^2 \dots \dots \dots + u_n^2) \dots \dots \dots (3) \text{ (since } P = F/A \text{ and } A = l^2)$$

Similarly, if P_y and P_z are the pressures on faces EFBA and FBCH, then

$$P_y = \frac{F_y}{l^2} = \frac{m}{l^3}(v_1^2 + v_2^2 + v_3^2 \dots \dots \dots + v_n^2) \dots \dots \dots (4)$$

$$P_z = \frac{F_z}{l^2} = \frac{m}{l^3}(w_1^2 + w_2^2 + w_3^2 \dots \dots \dots + w_n^2) \dots \dots \dots (5)$$

As the pressure exerted by the gas is same in all directions, the average pressure P of the gas is

$$P = \frac{P_x + P_y + P_z}{3} \dots \dots \dots (6)$$

$$P = \frac{m}{3l^3}(u_1^2 + u_2^2 + u_3^2 \dots \dots \dots + u_n^2) + (v_1^2 + v_2^2 + v_3^2 \dots \dots \dots + v_n^2) + (w_1^2 + w_2^2 \dots \dots \dots + w_n^2)$$

$$P = \frac{m}{3l^3}(u_1^2 + v_1^2 + w_1^2) + (u_2^2 + v_2^2 + w_2^2) \dots + (u_n^2 + v_n^2 + w_n^2) \dots \dots (7)$$

Since $l^3 = V$, the volume of the cube and $c_1^2 = u_1^2 + v_1^2 + w_1^2$

$$c_2^2 = u_2^2 + v_2^2 + w_2^2 \text{ and so on.}$$

$$P = \frac{m}{3V}(c_1^2 + c_2^2 + c_3^2 + \dots \dots \dots + c_n^2) \dots \dots (8)$$

or $P = \frac{1}{3} \frac{mn}{V} C^2$ where $C^2 = \frac{c_1^2 + c_2^2 + c_3^2 + \dots \dots \dots + c_n^2}{n}$ known as the mean square velocity of the molecules.

$$\text{If } M \text{ is the total mass of the gas, ie. } M = nm, \text{ then } P = \frac{1}{3} \frac{M}{V} C^2 \dots \dots (9)$$

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If ρ is the density of the gas, then pressure of the gas is $P = \frac{1}{3} \rho C^2$

C is called the root mean square velocity of the molecules and it is equal to the square root of the mean of the squares of the velocities of individual molecules.

It is given by $= \sqrt{\frac{3P}{\rho}}$.

To derive the relation $U = \frac{3}{2} R T$

The pressure exerted by a gas of n molecules occupying volume V is given by

$$P = \frac{1}{3} \frac{m n}{V} C^2 \quad \text{or} \quad P V = \frac{1}{3} m n C^2$$

If V is the volume occupied by a gram molecule of the gas and M is the molecular weight of the gas, then $M = m N_A$ where N_A is the Avogadro number.

$$P V = \frac{1}{3} M C^2 \dots\dots(1)$$

From the perfect gas equation $P V = R T$ (2)

From (1) and (2) we get $\frac{1}{3} M C^2 = R T$

$$\text{or } M C^2 = 3 R T$$

Dividing the above equation on both the sides by 2 we get $\frac{1}{2} M C^2 = \frac{3}{2} R T$ (3)

or $U = \frac{3}{2} R T$ (4) where $U = \frac{1}{2} M C^2$ is called the internal energy of the gas.

Dividing both sides of equation (3) by N_A , which is the number of molecules in one gram molecule of the gas or one mole, called Avogadro number, we get $\frac{1}{2} \frac{M}{N_A} C^2 = \frac{3}{2} \frac{R}{N_A} T$

As $M/N_A = m$ and $R/N_A = k$, where k is Boltzmann constant.

$$\frac{1}{2} m C^2 = \frac{3}{2} k T \quad \dots\dots(5)$$

Thus the mean kinetic energy per molecule in a given mass of gas is proportional to the absolute temperature of the gas.

Deduction of perfect gas equation

From kinetic theory of gases, the expression for pressure of a gram molecule of the gas is

$$P = \frac{1}{3} \frac{m n}{V} C^2 \quad \text{or} \quad P V = \frac{1}{3} m N_A C^2 \dots\dots(1)$$

$$\text{Or } P V = \frac{2}{3} \times \frac{1}{2} m N_A C^2 = \frac{2}{3} N_A \times \frac{1}{2} m C^2 \dots\dots(2)$$

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The average kinetic energy of 1 gram molecule of a gas at absolute temperature T is given by

$$KE = \frac{1}{2} M C^2 = \frac{1}{2} m N_A C^2$$

Average kinetic energy of a molecule is $\frac{1}{2} m C^2 = \frac{3}{2} k T$ (3)

Comparing equations (2) and (3) $P V = \frac{2}{3} N_A \times \frac{3}{2} k T$

or $P V = N_A k T$ or $P V = R T$ where $R = N_A k$

R is called universal gas constant given by $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

Derivation of Gas laws

(1) **Boyle's law** - From the kinetic theory of gases, the pressure exerted by a gas is given by

$$P = \frac{1}{3} \frac{M}{V} C^2 \quad \text{or} \quad P V = \frac{1}{3} M C^2$$

At a constant temperature C^2 is a constant. Thus for a given mass of a gas, from the above equation, $P V = \text{constant}$. Hence Boyle's law.

(2) **Charle's law** - The pressure of a gas is $P = \frac{1}{3} \frac{M}{V} C^2$ or $V = \frac{1}{3} \frac{m n}{P} C^2$

Thus for a given mass of gas, at constant pressure $V \propto C^2$

As $C^2 \propto T$, we get $V \propto T$. Hence the Charle's law.

Similarly it can be shown that $P \propto T$ at constant volume called the Regnault's law.

(3) **Avogadro's law** - This law states that at the same temperature and pressure equal volumes of all gases contain the same number of molecules.

Let n_1 and n_2 be the number of molecules of two different gases, m_1 and m_2 their masses and C_1 and C_2 the respective root mean square velocities. Since the two gases have the same pressure and for unit volume the gases,

$$P = \frac{1}{3} m_1 n_1 C_1^2 = \frac{1}{3} m_2 n_2 C_2^2 \quad \dots\dots(1)$$

As the temperature of the two gases are same, there is no change in temperature when they are mixed. This is possible only if the mean kinetic energy per molecule in the two gases is the same. ie. $\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 \dots(2)$

Based on the equation (2) equation (1) reduces to the condition $n_1 = n_2$. Hence the Avogadro law.

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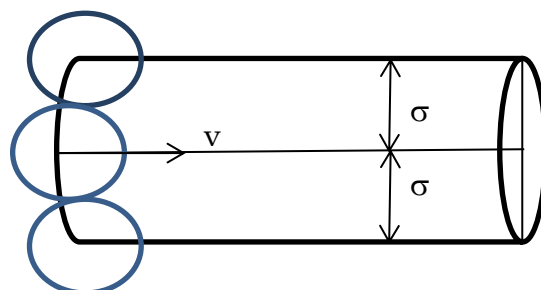
Mean free path

The average distance travelled by a molecule in a gas between any two successive collisions is called mean free path of the molecule. It is denoted by λ .

If the total path travelled in N collisions is S , then the mean free path is given by $\lambda = \frac{S}{N}$

Expression for mean free path

Consider n as the number of molecules per unit volume of a gas and let σ be the diameter of each of these molecules.



The assumption made here is that only the molecule under consideration is in motion, while all other molecules are at rest.

The moving molecule will collide with all those molecules whose centres lie within a distance σ from its centre as shown in the figure.

If v is the velocity of the molecule, in one second it will collide with all the molecules the centres of which lie in a cylinder of radius σ and length v , and hence in a volume $\pi\sigma^2 v$.

The number of molecules in this cylindrical volume is $\pi\sigma^2 v n$.

Thus the number of collisions N made by the moving molecule is also $\pi\sigma^2 v n$.

or $N = \pi\sigma^2 v n$.

As the distance S traversed by the molecule in one second is its velocity v , the mean free path λ

is given by $\lambda = \frac{S}{N} = \frac{v}{\pi\sigma^2 v n} = \frac{1}{\pi\sigma^2 n}$

Thus $\lambda = \frac{1}{\pi\sigma^2 n}$ (1) This equation connecting the mean free path with the molecular diameter and the number of molecules per unit volume was deduced by Clausius.

Boltzmann, assuming that all the molecules have the same average speed deduced the equation

$$\lambda = \frac{3}{4\pi\sigma^2 n} \dots\dots\dots(2)$$

Maxwell, based on the exact law of distribution of velocities, obtained a more correct equation

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n} \dots\dots\dots(3)$$

From the above equation it is clear that mean free path is inversely proportional to the square of the molecular diameter.

From the perfect gas equation $P V = R T$ or $P V = N_A k T$ where $R = N_A k$

$$\text{We get } P = \frac{N_A k T}{V} = n k T \quad \text{or } n = \frac{P}{k T}$$

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Substituting for n in equation (3) $\lambda = \frac{kT}{\sqrt{2} \pi \sigma^2 P}$. Thus mean free path is directly proportional to the absolute temperature and inversely proportional to the pressure.

Maxwell's law of distribution of velocity among the molecules

The molecules of a gas are in random motion. There is a continuous change in the magnitude and direction of their velocities (speeds) due to random motion and collisions between the molecules. Maxwell analysed the distribution of velocities by the statistical method.

Maxwell's law - According to this law, the number of molecules (dn) possessing velocities between c and c + dc is given by

$$dn = 4 \pi n a^3 e^{-b c^2} c^2 dc \quad \dots\dots\dots(1)$$

Where n is the number of molecules per unit volume and $a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2 \pi k T}}$

Relation (1) is called Maxwell's law of distribution of velocities.

let $b c^2 = x^2$, differentiating $2bc dc = 2x dx$ or $dc = x dx/bc$

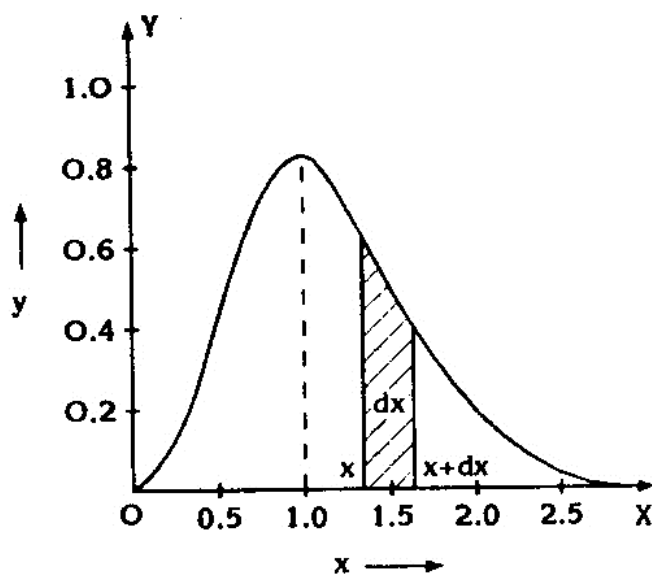
Also $a = \sqrt{\frac{b}{\pi}}$ Thus $a^3 = \left(\frac{b}{\pi}\right)^{3/2}$ Also $c = \sqrt{b} x$

Substituting the above terms in equation (1) we get

$$\frac{dn}{n} = 4 \pi \left(\frac{b}{\pi}\right)^{3/2} e^{-x^2} \frac{x}{bc} dx$$

Simplifying the above equation $\frac{dn}{n} =$

Plotting Maxwell speed distribution function y versus x ($y = f(v) = dn/n$ and x the molecular speed) we get the graph as shown.



$$4 \pi^{-1/2} e^{-x^2}$$

1. The shaded region between x and x + dx gives the total number of molecules (dn/n) whose velocities lie between c and c + dc.
2. The area under the graph gives the total number of molecules n with velocities between zero and infinity.
3. The co ordinate y corresponding to any value of x gives the number of molecules having velocity represented by x.
4. dn/n is maximum at x = 1 which represents the most probable velocity.

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To find root mean square (rms) velocity

Let dn be the number of molecules having velocities between c and $c + dc$. If n is the total number of molecules, the mean square velocity is

$$c_{ms}^2 = \frac{1}{n} \int_0^{\infty} c^2 dn \quad \text{As } \frac{dn}{n} = 4 \pi a^3 e^{-b c^2} c^2 dc$$

$$c_{ms}^2 = 4 \pi a^3 \int_0^{\infty} e^{-b c^2} c^4 dc = 4 \pi a^3 \frac{3}{8 b^2} \sqrt{\frac{\pi}{b}}$$

where the standard integral used is $\int_0^{\infty} e^{-b c^2} c^4 dc = \frac{3}{8 b^2} \sqrt{\frac{\pi}{b}}$

By simplifying the above equation, we get $c_{ms}^2 = 4 \pi \left(\frac{b}{\pi}\right)^{3/2} \frac{3}{8 b^2} \sqrt{\frac{\pi}{b}} = \frac{3}{2 b}$

The root mean square velocity $c_{rms} = \sqrt{c_{ms}^2} = \sqrt{\frac{3}{2 b}}$

As $b = \frac{m}{2 k T}$ we get $c_{rms} = \sqrt{\frac{3 k T}{m}} = 1.732 \sqrt{\frac{k T}{m}} \dots\dots\dots(1)$

To find mean or average velocity

The average velocity of the molecule is $\bar{c} = \frac{1}{n} \int_0^{\infty} c dn$

$$\bar{c} = 4 \pi a^3 \int_0^{\infty} e^{-b c^2} c^3 dc = 4 \pi a^3 \frac{1}{2 b^2}$$

where the standard integral used is $\int_0^{\infty} e^{-b c^2} c^3 dc = \frac{1}{2 b^2}$

$$\bar{c} = 4 \pi \left(\frac{b}{\pi}\right)^{3/2} \frac{1}{2 b^2} = \sqrt{\frac{8 k T}{\pi m}} \quad \text{Thus } \bar{c} = \sqrt{\frac{8 k T}{\pi m}} = 1.596 \sqrt{\frac{k T}{m}} \dots\dots(2)$$

To find most probable velocity

It is the velocity possessed by maximum number of molecules in the gas.

Therefore the probability of molecules having velocities in the range c and $c + dc$ must be

maximum or $\frac{d}{dc} \left(\frac{dn}{n}\right) = 0$

$$\frac{d}{dc} (4 \pi a^3 e^{-b c^2} c^2 dc) = 0$$

$$4 \pi a^3 (e^{-b c^2} 2c - c^2 e^{-b c^2} 2bc) = 0$$

$$4 \pi a^3 2c e^{-b c^2} (1 - b c^2) = 0$$

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$$\text{or } 1 - b c^2 = 0 \quad \text{or } c^2 = \frac{1}{b}. \quad \text{Thus } c_{mp} = \sqrt{\frac{1}{b}} = \sqrt{\frac{2kT}{m}}$$

$$\text{or } c_{mp} = \sqrt{\frac{2kT}{m}} = 1.414 \sqrt{\frac{kT}{m}} \quad \dots(3)$$

Comparison of the three equations shows

$$c_{mp} : \bar{c} : c_{rms} = 1.414 : 1.596 : 1.732 \quad \text{Thus } c_{mp} < \bar{c} < c_{rms}$$

Degrees of freedom

It is defined as the number of independent variables required to specify the position and configuration of a molecule completely. It is also the number of independent components of velocities needed to describe the motion of molecules completely.

The degrees of freedom of the system is given by $f = 3N - r$ where N is the number of particles in the system and r is the number of independent relations among the particles.

A monoatomic gas (one atom per molecule like neon, argon, helium etc..) has only three translational kinetic energy along the three coordinate axes x , y and z . Thus $N = 1$ and $r = 0$. $f = 3$. (three degrees of freedom)

A diatomic gas (two atoms per molecule like N_2 , O_2 , H_2 , CO etc...) has both translational and rotational kinetic energies. If there are rotational kinetic energy along two perpendicular axes along with three translational kinetic energy, then $N = 2$ and $r = 1$. Thus $f = 5$. (five degrees of freedom)

A triatomic (three atoms per molecule like, H_2S , H_2O , SO_2) or polyatomic gas there are three translational and three rotational kinetic energies or degrees of freedom for a non linear molecule. Thus $N = 3$ and $r = 3$. This give $f = 6$.

For triatomic linear molecule like CO_2 , CS_2 , HCN , two atoms lie along the side of the central atom. $N = 3$, $r = 2$ and $f = 7$.

Principle of Equipartition of energy

Statement According to this law, the total energy of a dynamic system in thermal equilibrium is shared equally by all its degrees of freedom, the energy associated per molecule per degree of freedom being a constant equal to $\frac{1}{2} kT$ where k is the Boltzmann constant and T is the absolute temperature of the system.

Consider one mole of a monoatomic gas in thermal equilibrium at temperature T . It has three degrees of freedom. According to the Maxwell's theory of equipartition of energy in the steady

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state, $\overline{u^2} = \overline{v^2} = \overline{w^2}$ where \bar{u} , \bar{v} and \bar{w} are the average values of the component velocities of a molecule.

$$\text{As } c^2 = \overline{u^2} + \overline{v^2} + \overline{w^2} \quad \text{Thus } \overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3} c^2$$

$$\text{Thus } \frac{1}{2} m \overline{u^2} = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m \overline{w^2} = \frac{1}{3} \frac{1}{2} m c^2$$

According to kinetic theory of gases, the average kinetic energy of a gas molecule is $\frac{1}{2} m c^2 = \frac{3}{2} k T$

$$\text{Thus } \frac{1}{2} m \overline{u^2} = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m \overline{w^2} = \frac{1}{3} \frac{3}{2} k T = \frac{1}{2} k T$$

Therefore, the average kinetic energy per degree of freedom is equal to $\frac{1}{2} k T$.

Derivation of $U = \frac{3}{2} R T$

According to the equipartition of energy, the average kinetic energy associated with each degree of freedom is equal to $\frac{1}{2} k T$ where k is the Boltzmann constant and T is the absolute temperature.

The energy associated with the three degrees of freedom is equal to $\frac{3}{2} k T$.

The energy associated with one gram molecule of a gas is given by

$$U = N_A \times \frac{3}{2} k T = \frac{3}{2} (N_A k) T$$

Thus $U = \frac{3}{2} R T$ where $R = N_A k$ and U is the internal energy.

Specific heat of gases

For a monoatomic gas, the total energy U of 1 gram molecule of the gas at the absolute temperature T is given by $U = 3 \times \frac{1}{2} k T \times N_A = \frac{3}{2} R T$

If C_V is the molecular specific heat at constant volume, (the quantity of heat required to raise one gram molecule through one degree), then

$$C_V = \frac{dU}{dT} = \frac{3}{2} R \quad \dots\dots(1)$$

If C_P is the molecular specific heat at constant pressure, then $C_P - C_V = R$

$$C_P = C_V + R = \frac{5}{2} R \quad \dots\dots(2)$$

From (1) and (2) it is observed that molecular specific heats of monoatomic gas are constants independent of the temperature and nature of the gas.

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The theoretical predictions agree with the experimental results.

For a diatomic gas $U = \frac{5}{2} R T$. Hence $C_V = \frac{dU}{dT} = \frac{5}{2} R$ and $C_P = \frac{7}{2} R$.

For triatomic or polyatomic gas, $U = \frac{6}{2} R T$. Hence $C_V = \frac{dU}{dT} = 3 R$ and $C_P = 4 R$.

Ratio of specific heat of gases

The ratio of specific heat of a gas at constant pressure to the specific heat at constant volume is called the atomicity of the gas denoted by $\gamma = \frac{C_P}{C_V}$

For a monoatomic gas $\gamma = \frac{C_P}{C_V} = \frac{\left(\frac{5}{2}\right)R}{\left(\frac{3}{2}\right)R} = \frac{5}{3} = 1.67$

For a diatomic gas $\gamma = \frac{C_P}{C_V} = \frac{\left(\frac{7}{2}\right)R}{\left(\frac{5}{2}\right)R} = \frac{7}{5} = 1.41$

For a polyatomic gas $\gamma = \frac{C_P}{C_V} = \frac{4R}{3R} = \frac{4}{3} = 1.33$

Importance of γ - (1) Its value lies between 1 and 1.67, (2) It gives the atomicity of a molecule, (3) Its value decreases with increasing atomicity and (4) It helps in finding the molecular structure of the gas.

Relation between γ and degrees of freedom

The average kinetic energy per molecule is $\frac{1}{2} f k T$

The total energy associated with 1 mole of the gas for f degrees of freedom is $U = \frac{1}{2} f k T N_A = \frac{1}{2} f R T$

$$C_V = \frac{dU}{dT} = \frac{f}{2} R \dots\dots(1)$$

If C_P is the molecular specific heat at constant pressure, then $C_P - C_V = R$

$$C_P = C_V + R = \left(\frac{f}{2} + 1\right) R \dots\dots(2)$$

$$\text{Thus } \gamma = \frac{C_P}{C_V} = \frac{\left(\frac{f}{2} + 1\right)R}{\frac{f}{2}R} = \frac{2}{f} \left(\frac{f}{2} + 1\right) \text{ or } \gamma = 1 + \frac{2}{f}$$

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Real gases

Gases obeying the gas laws (Boyle's law, charle's law, perfect gas equation) at all temperatures and pressures are called the perfect or the ideal gases. Gases which do not obey the gas laws are called real gases.

Study on the properties of vapours indicated that deviations from gas laws applicable to ideal gases was intimately connected with the process of liquefaction of a gas, as the deviation become more marked when the gas was nearing liquefaction.

Andrew's experiment on carbon dioxide

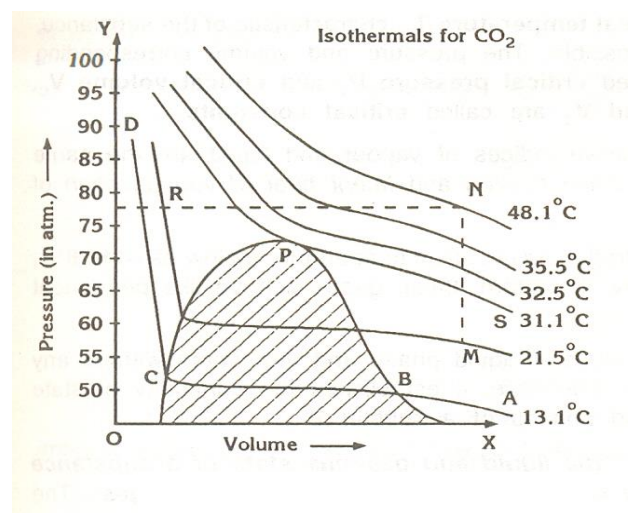
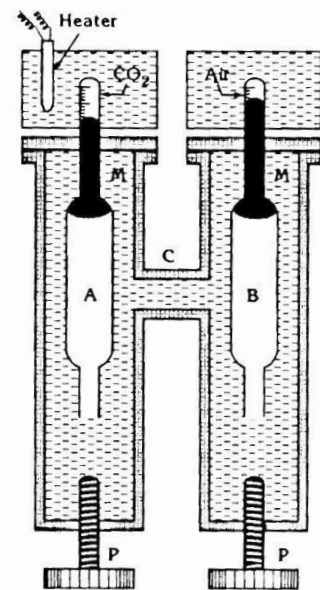
Principle - The principle involved in this experiment is to measure the volume of a fixed mass of the gas at various pressures at a given temperature and draw curves of variation of pressure with volume called isothermals. From this it is possible to investigate the deviation of a gas from Boyle's law.

Apparatus - Andrews' apparatus consist of two identical tubes A and B, initially open at both the ends, with thickwalled capillary at the upper side. The capillary tubes are graduated to measure their volume and length correctly.

Carbon dioxide is passed through tube A for a long time and its two ends are properly sealed. Then the lower end of the tube is immersed in mercury and opened. When the tube is warmed and allowed to cool, a small column of mercury (M) enters the tube and encloses the gas in the capillary portion of the tube.

To measure pressure, tube B is enclosed with dry air above the mercury column. The two tubes are mounted side by side inside two big copper cylinders as shown in figure.

Procedure - The copper cylinders are filled with water. The water in the cylinders is in communication through C and the pressure is equalized. The lower end of the copper cylinders are provided with screw plungers (S). When the plungers are turned, the gases are forced into the capillaries and are compressed and both carbon



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dioxide and dry air are subjected to high pressures. The projecting portions of the capillaries are enclosed in two separate water baths, one around B is maintained at constant temperature and that around A can be maintained between 0°C to 100°C .

The plungers (S) are turned into the cylinders to increase pressure. Then the volume of the gas and that of dry air are measured from the graduations on A and B. Maintaining the temperature of CO_2 at a particular value, the volume of the gas is measured at different pressures. This is repeated for different constant temperatures of the gas. The graphs between pressures and volumes of carbon dioxide are drawn called isothermals as shown.

Interpretation of the isothermals

1. At 13.1°C , the isothermal starts from A. Till B it obeys Boyle's law representing gaseous state. B to C indicates liquefaction in which liquid and vapour are in equilibrium. CD indicates purely liquid state.
2. At 21.5°C , the horizontal portion is shorter, i.e. Vapour liquid region is smaller.
3. At 31.1°C the horizontal portion is just a point, called the point of inflexion or critical point and the isothermal is called critical isothermal. The corresponding temperature is called critical temperature. The gas cannot be liquefied above this temperature even at high pressure.
4. At higher temperatures, the behaviour of the graph is that of a permanent gas and obeys Boyle's law.

Results of Andrew's experiment

1. For every substance there is a critical temperature T_C above which liquefaction is not possible. The corresponding pressure and volume is called critical pressure P_C and V_C respectively. These values are called **critical constants**.
2. At T_C the densities and refractive indices are the same for the liquid and vapour. But the surface tension and latent heat of vapourisation of the liquid are zero.
3. Gases like oxygen, nitrogen and hydrogen have T_C as low as -118.8°C , -147.1°C and -239.9°C respectively.
4. Andrew concluded that liquid and gaseous state of a substance are only the distinct stages of a long series of continuous physical changes.

Van der Waals' equation of state

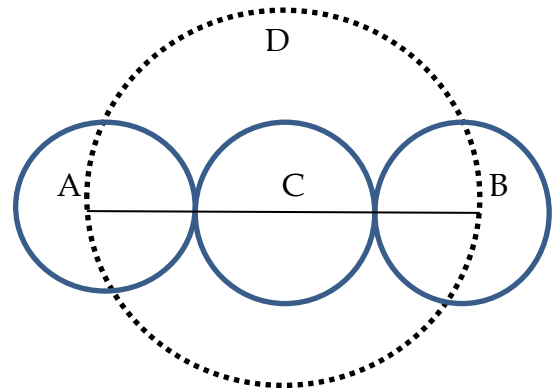
The two fundamental assumptions of kinetic theory of gases are (1) the molecules are point masses having no dimensions and (2) no intermolecular forces exist between the

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molecules, had justified the perfect gas equation in case of ideal gases.

Experiments like Andrew's experiment and Joule Thomson effect have shown that real gases or actual gases deviated from the perfect gas equation. The deviation being small at low pressure and high temperature, large at high pressure and low temperature.

Van der waals' said that the modification in the perfect gas equation to cover real gases requires the changes in assumptions in kinetic theory of gases. Accordingly, the finite size of the molecules and intermolecular forces between the molecules cannot be neglected and must be considered.



1 Correction for finite size of the molecule

Consider V to be the volume occupied by a gas having molecules each of diameter σ . As the molecules are assumed to be solid spheres, every molecule has a sphere of influence into which other molecules cannot enter. D is the sphere of influence of molecule C of radius σ which is the diameter of a molecule.

The volume of the sphere D is $V_S = \frac{4}{3} \pi \sigma^3$

The volume of a molecule $V_m = \frac{4}{3} \pi \left(\frac{\sigma}{2}\right)^3 = \frac{1}{8} \left(\frac{4}{3} \pi \sigma^3\right)$

Thus $V_m = \frac{V_S}{8}$ or $V_S = 8 V_m$ (1)

If V is the volume available for the first molecule, then the volume available for the second molecule is $V - V_S$.

Thus the volume available for the n th molecule is $V - (n - 1) V_S$.

The average volume available for each molecule is $V - \frac{V_S(1+2+\dots+(n-1))}{n}$

$$= V - \frac{V_S}{n} \times \frac{n(n-1)}{2} \left[\because 1 + 2 + \dots + (n-1) = \frac{n(n-1)}{2} \right]$$

$$= V - \frac{n V_S}{2} + \frac{V_S}{2}$$

$$= V - n \frac{V_S}{2} \left[\because \frac{V_S}{2} < \frac{n V_S}{2} \right] \frac{V_S}{2}$$

$$= V - \frac{n}{2} 8 V_m \quad \text{or} \quad \text{average volume} = V - 4 n V_m = V - b$$

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where $b = 4 n V_m$. Substituting for average volume in ideal gas equation $P V = R T$, we get
 $P (V - b) = R T$ (2)

2 Correction for intermolecular attraction

A molecule of the gas present deep inside the gas experience zero force as it is pulled by other molecules around it with same force. But a molecule near the wall of vessel containing the gas, experiences net inward force pulling the molecule back, away from the wall. Thus the velocity and momentum of the molecule impinging on the wall decreases. The resultant pressure exerted by the gas on the wall of the container is less as compared to that in the absence of intermolecular forces.

Therefore, the decrease in pressure depends on (1) the number of molecules striking unit area of the walls of the vessel and (2) the number of molecules attracting them backwards. Each of these factors depend on the density ρ of the gas.

Thus the decrease in pressure is directly proportional to ρ^2

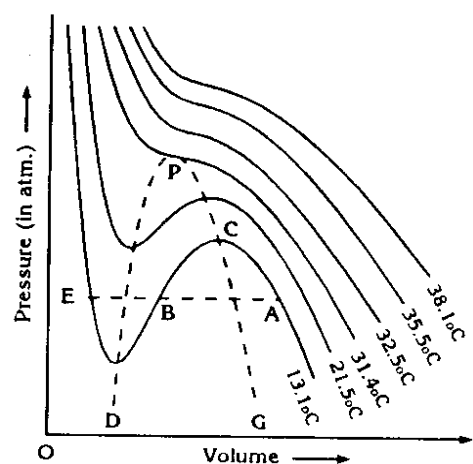
For a given mass density is inversely proportional to the volume of the gas. Thus decrease in pressure $\propto \frac{1}{V^2}$

or decrease in pressure is equal to $\frac{a}{V^2}$ where a is a constant.

Therefore the correct pressure exerted by the gas in the absence of intermolecular attraction is obtained by adding this term to the reduced pressure P i.e. $(P + \frac{a}{V^2})$. Substituting this in equation (2) we get $(P + \frac{a}{V^2})(V - b) = R T$. This equation is called the **Van der Waals' equation of state**. The graph showing the variation of P with V plotted using van der waals equation is as shown.

Comparison between the graphs of Andrew's experiment and the van der waals equation - Similarities

- 1 The graphs are similar at higher temperatures.
- 2 At lower temperatures the curved portions are sharper in both the graphs.
- 3 At 31.1°C, both the graphs show horizontal tangent indicating the critical temperature.
- 4 At lower temperatures the gas does not behave as a perfect gas.



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Dissimilarities

- 1 Below the critical temperature, van der waal curve show turning point whereas Andrew curve show horizontal position.
- 2 In the van der waal curve, the regions AC and DE represent unstable, supercooled and super heated liquid states respectively and region CBD show decrease in pressure which has no meaning.

Expression for critical constants

The limiting temperature at which a gas can be liquified by increasing pressure only and above which it cannot be liquefied is called **critical temperature T_C** .

The pressure applied to the gas at critical temperature so that gas can be liquefied is called **critical pressure P_C** .

The volume of the gas at critical temperature so that gas can be liquefied is called **critical volume V_C** .

The critical temperature and the corresponding values of pressure and volume at the critical point are called **critical constants**.

Consider the Van der Waals' equation $\left(P + \frac{a}{V^2}\right)(V - b) = R T \dots(1)$

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

Differentiating equation (2) $\frac{dP}{dV} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \dots\dots(3)$

At critical point, the rate of change of pressure with volume is zero

ie. $\frac{dP}{dV} = 0$ and also $\frac{d^2P}{dV^2} = 0$. Also $T = T_C$ and $V = V_C$

Equation (3) reduces to $0 = -\frac{RT_C}{(V_C-b)^2} + \frac{2a}{V_C^3}$

or $\frac{2a}{V_C^3} = \frac{RT_C}{(V_C-b)^2} \dots\dots(4)$

Differentiating (3) with respect to V again

$$\frac{d^2P}{dV^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

At critical point $\frac{d^2P}{dV^2} = 0$, thus, $0 = \frac{2RT_C}{(V_C-b)^3} - \frac{6a}{V_C^4}$

or $\frac{3a}{V_C^4} = \frac{RT_C}{(V_C-b)^3} \dots\dots(5)$

Dividing (4) by (5) we get $\frac{2V_C}{3} = V_C - b$ or $V_C = 3b \dots(6)$

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Substituting for V_C from (6) in (4) $\frac{2a}{(3b)^3} = \frac{RT_C}{(3b-b)^2}$

Or $T_C = \frac{8a}{27Rb}$ (7)

Substituting for V_C and T_C from (6) and (7) in (2)

$P_C = \frac{R}{(3b-b)} \times \frac{8a}{27Rb} - \frac{a}{9b^2}$ or $P_C = \frac{a}{27b^2}$ (8)

The expressions for the critical constants are

$P_C = \frac{a}{27b^2}$, $T_C = \frac{8a}{27Rb}$ and $V_C = 3b$

Coefficients of Van der waals' constants or critical constants

Dividing the expression for T_C by P_C $\frac{T_C}{P_C} = \frac{8a}{27Rb} \times \frac{27b^2}{a} = \frac{8b}{R}$

Thus $b = \frac{RT_C}{8P_C}$

Substituting for b in the equation for T_C $T_C = \frac{8a}{27R} \times \frac{8P_C}{RT_C}$

Thus $a = \frac{27R^2T_C^2}{64P_C}$

The critical coefficient of the gas is given by $\frac{RT_C}{P_C V_C}$. Its value is equal to $\frac{8}{3}$. This value is same for all gases.

Limitations of van der waals equation

1. According to van der waals equation the critical coefficient is $8/3$. But experimentally it varies from 3.27 to 4.99.
2. The value of b must be theoretically is $V_C/3$. But experimentally its value is $V_C/2$.
3. The isothermals obtained theoretically from van der waals equation do not agree with the isothermals found from Andrews experiment.
4. The value of a and b do not remain constant at all temperatures even for the same gas.

Differences between Ideal gases and Real gases

S. No.	Ideal gas	Real gas
1	Obeys Boyles' law, Charles' law and perfect gas equation $PV = RT$	Does not obey Boyles' law, Charles' law and perfect gas equation
2	Equation of state $PV = RT$	$\left(P + \frac{a}{V^2}\right)(V - b) = RT$

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3	Their specific heat is independent of temperature	Their specific heat is dependent on temperature $C_V \propto T$
4	Their internal energy depends only on temperature	Their internal energy depends on temperature as well as volume
5	At high temperatures and low pressures behave as ideal gas	At low temperature and high pressure behave as real gas

Transport Phenomenon

The phenomenon that can be explained on the basis of movement of molecules of a gas is called transport phenomenon.

The phenomenon of viscosity and thermal conductivity take place due to the transfer of momentum and transfer of heat energy respectively.

Viscosity of gases

When different layers of a fluid have different velocities, in order to attain steady state, momentum is transferred from faster moving molecules to slower moving molecules. This phenomenon is called viscosity.

Consider a gas moving over a horizontal solid surface. The gas is imagined to be made up of different layers, having velocity gradient $\frac{dv}{dy}$ with increasing velocities with distance from the surface.

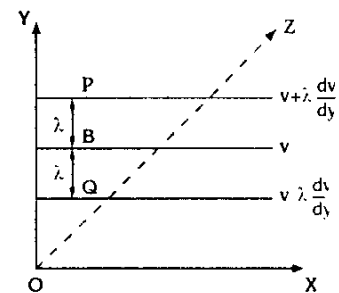
Thus, a relative motion exists between layers of the fluid resulting in opposing force between them. This force is $F = \eta \frac{dv}{dy}$ (1)

where η is called the coefficient of viscosity.

Consider different layers of fluid as shown in the diagram. Let $n = \frac{N}{V}$ be the number of molecules per unit volume and \bar{c} be their average velocity.

Due to thermal agitation, the molecules move in all possible directions. If the three coordinate axes are considered with both positive and negative directions, the number of molecules crossing unit area of layer B in one second in any one direction is (ie. upwards or downwards) $= \frac{1}{6} n \bar{c}$. The mass of these molecules $M = \frac{1}{6} n \bar{c} m$ where m is mass of each molecule.

Let P and Q be the two layers of gas at distance λ called mean free path on either side of layer B between which the molecules do not collide with each other. Let v be the velocity of gas in layer B.



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The velocity of gas in layer P = $v + \lambda \frac{dv}{dy}$

The velocity of gas in layer Q = $v - \lambda \frac{dv}{dy}$

The momentum transferred from P to Q per unit area of the plane B per second is given by

$$P_1 = M \times \left(v + \lambda \frac{dv}{dy} \right) = \frac{1}{6} nm \bar{c} \left(v + \lambda \frac{dv}{dy} \right)$$

Similarly the momentum transferred from Q to P per unit area of plane B per second is given by

$$P_2 = M \times \left(v - \lambda \frac{dv}{dy} \right) = \frac{1}{6} nm \bar{c} \left(v - \lambda \frac{dv}{dy} \right)$$

Thus change in momentum per unit area per second is $\Delta P = P_1 - P_2$

$$\Delta P = \frac{1}{6} nm \bar{c} \left\{ \left(v + \lambda \frac{dv}{dy} \right) - \left(v - \lambda \frac{dv}{dy} \right) \right\}$$

$$\text{or } \Delta P = \frac{1}{6} nm \bar{c} \left\{ 2\lambda \frac{dv}{dy} \right\}$$

This term is equal to force F from Newton's second law. Thus $F = \frac{1}{3} nm \bar{c} \lambda \frac{dv}{dy}$ (2)

Comparing equations (1) and (2) we get $\eta \frac{dv}{dy} = \frac{1}{3} nm \bar{c} \lambda \frac{dv}{dy}$

Or $\eta = \frac{1}{3} nm \bar{c} \lambda$ Also $\rho = \frac{\text{mass}}{\text{volume}} = nm$ where $n = \frac{N}{V}$.

Thus $\eta = \frac{1}{3} \rho \bar{c} \lambda$ As $\lambda = \frac{1}{\sqrt{2} n \pi \sigma^2}$, $\eta = \frac{1}{3} n m \bar{c} \frac{1}{\sqrt{2} n \pi \sigma^2} = \frac{m \bar{c}}{3\sqrt{2} \pi \sigma^2}$

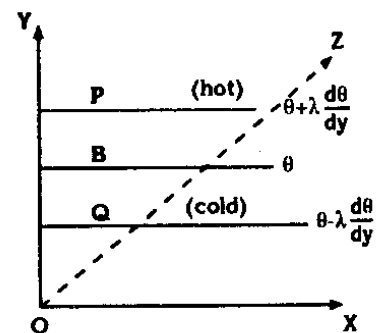
Thus the coefficient of viscosity depends on mass, velocity and diameter of the molecules.

As $\bar{c} \propto \sqrt{T}$, $\eta \propto \sqrt{T}$

Thermal conductivity of gases

When different layers of a fluid have different temperatures, in order to attain steady state, heat energy is transferred from higher temperature layer to lower temperature layer. This phenomenon is called thermal conduction.

Consider a gas moving over a horizontal solid surface. The gas is imagined to be made up of different layers, having temperature gradient $\frac{dT}{dy}$ with increasing temperatures with distance from the surface.



Thus, there is a heat transfer from a layer of higher temperature to the layer of lower temperature. If Q is the transfer of heat per unit area per second then $Q = K \frac{dT}{dy}$ (1)

where K is called the coefficient of thermal conductivity.

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Consider different layers of fluid as shown in the diagram. Let $n = \frac{N}{V}$ be the number of molecules per unit volume and \bar{c} be their average velocity.

Due to thermal agitation, the molecules move in all possible directions. If the three coordinate axes are considered with both positive and negative directions, the number of molecules crossing unit area of layer B in one second in any one direction is (ie. upwards or downwards) $= \frac{1}{6} n \bar{c}$. The mass of these molecules is $M = \frac{1}{6} n \bar{c} m$ where m is mass of each molecule.

Let P and Q be the two layers of gas at distance λ called mean free path on either side of layer B between which the molecules do not collide with each other. Let T be the temperature of layer B. The temperature of gas in layer P $= T + \lambda \frac{dT}{dy}$

The temperature of gas in layer Q $= T - \lambda \frac{dT}{dy}$

The heat transferred from P to Q per unit area of plane B per second is given by

$$Q_1 = M C_V \times \left(T + \lambda \frac{dT}{dy} \right) = \frac{1}{6} nm C_V \bar{c} \left(T + \lambda \frac{dT}{dy} \right)$$

Similarly the heat transferred from Q to P per unit area of plane B per second is given by $Q_2 =$

$$M C_V \times \left(T - \lambda \frac{dT}{dy} \right) = \frac{1}{6} nm C_V \bar{c} \left(T - \lambda \frac{dT}{dy} \right)$$

where C_V is the specific heat of gas at constant volume. Thus change in heat per unit area per second is $\Delta Q = Q_1 - Q_2$

$$\Delta Q = \frac{1}{6} nm C_V \bar{c} \left\{ \left(T + \lambda \frac{dT}{dy} \right) - \left(T - \lambda \frac{dT}{dy} \right) \right\}$$

$$\text{or } \Delta Q = \frac{1}{6} nm C_V \bar{c} \left\{ 2\lambda \frac{dT}{dy} \right\}$$

This term is equal to net heat energy Q transferred. Thus $Q = \frac{1}{3} nm C_V \bar{c} \lambda \frac{dT}{dy}$ (2)

Comparing equations (1) and (2) we get $K \frac{dT}{dy} = \frac{1}{3} nm C_V \bar{c} \lambda \frac{dT}{dy}$

Or $K = \frac{1}{3} nm C_V \bar{c} \lambda$ Also $\rho = \frac{\text{mass}}{\text{volume}} = nm$ where $n = \frac{N}{V}$.

Thus $K = \frac{1}{3} \rho C_V \bar{c} \lambda$

Thus the coefficient of thermal conductivity is independent of pressure and directly proportional to the temperature. (As $\bar{c} \propto \sqrt{T}$, $K \propto \sqrt{T}$)

Note : Relation between η and K

As $\eta = \frac{1}{3} \rho \bar{c} \lambda$ and $= \frac{1}{3} \rho C_V \bar{c} \lambda$. Thus $K = \eta C_V$

