KINETIC THEORY AND THE IDEAL GAS

Thermodynamics

The branch of Physics which deals with the conversion of heat energy into mechanical energy and vice versa is called thermodynamics.

Temperature

It is the degree of hotness or coldness of a body.

It may also be defined as:

A physical property of the body which determines the direction of flow of heat from one body to the other, when they are brought in thermal contact.

State Variables (Thermodynamic Coordinates)

The physical quantities which describe the state of a system are called state variables or thermodynamic coordinates e.g., pressure, volume, temperature, internal energy, entropy etc.

Ideal Gas

The gas which obeys gas laws under all temperatures and pressures is called an ideal gas. The molecules of an ideal gas have no potential energy but only K.E.

Ideal Gas Law

According to Boyle's law, volume V of gas is inversely proportional to its pressure P if its temperature is kept constant.

$$V \propto \frac{1}{P} \qquad \text{------------ (1)}$$

From Charles law, the volume V of gas is directly proportional to its absolute temperature T if its pressure is kept constant.

$$V \propto T \qquad \text{------------ (2)}$$

From Gay-Lussac's law, volume V of gas is directly proportional to number of molecules N if pressure and temperature are kept constant.

$$V \propto N \qquad \text{------------ (3)}$$

Combining (1), (2) and (3), we have:

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

$$\frac{PV}{T} \propto N$$

$$\frac{PV}{T} = constant \times N$$

$$\frac{PV}{NT} = k \qquad \text{------------ (4)}$$

Here k is constant called Boltzmann constant. It is a universal constant and its value is

$$k = 1.38066 \times 10^{-23} \, J/K$$

If n is the number of moles then $N = nN_A$. So equation (4) becomes:

$$\frac{PV}{nN_AT} = k$$

$$\frac{PV}{nT} = N_Ak$$

But $N_Ak = R$, here R is universal gas constant and is value is $R = 8.3145 \frac{J}{mol-K}$

$$\frac{PV}{nT} = R$$

$$PV = nRT$$

This equation is called ideal gas law.

Kinetic Theory of Gases

The kinetic theory of gas is based on following assumptions:

- The number of molecules in the gas is large, and the average separation between them is large compared with their dimensions.
- The molecules execute random motion and obey the Newton's laws of motion.
- The molecules make elastic collisions with each other and with the walls of container.
- The gas under consideration is a pure substance; that is, all molecules are identical.

Pressure of the Gas

       Consider an ideal gas in a cubical container having edge length L. Let m is the mass of one molecule of gas and N be the total number of molecules in the container. Let a molecule moves with velocity v and v_x, v_y and v_z are its rectangular components.
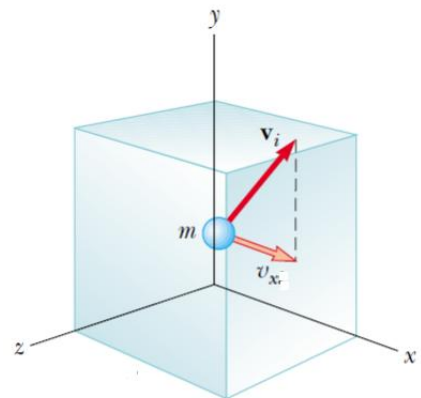
       Suppose the molecule moves from one face A_1 to face A_2 with velocity v_x and after collision with face its velocity becomes $-v_x$. Consider the molecule reaches face A_2 without any collision with other molecule on the way. After collision with A_2, the molecule goes back to face A_1.

$$Force\ exerted\ by\ a\ molecule\ on\ A_2 = \frac{Momentum\ Transferred\ to\ the\ face\ A_2}{Time\ between\ the\ successive\ collisions\ with\ A_1}$$ ---- (1)

As

$$Change\ in\ momentum\ = (Final\ Momentum) - (Initial\ Momentum)$$

$$= (-mv_x) - (mv_x) = -2mv_x$$

$$Momentum\ Transferred\ to\ A_2 = 2mv_x$$

And

The time taken by the molecule in moving from A_1 to A_2 and back to A_1 is $t = \dfrac{2L}{v_x}$. Putting values in equation (1), we get:

$$Force\ exerted\ by\ the\ molecule\ on\ face\ A_2 = \frac{2mv_x}{\left(\dfrac{2L}{v_x}\right)} = \frac{mv_x^2}{L}$$

This is the force exerted by one molecule on $face\ A_2$. Total impulsive force exerted on A_2 by all molecules is given by:

$$F_x = \frac{mv_{1x}^2}{L} + \frac{mv_{2x}^2}{L} + \dots\dots\dots + \frac{mv_{Nx}^2}{L}$$

$$F_x = \frac{m}{L}(v_{1x}^2 + v_{2x}^2 + \dots\dots\dots + v_{Nx}^2)$$

Now the pressure P of the gas will be:

$$P = \frac{F_x}{L^2} = \frac{1}{L^2} \times \frac{m}{L}(v_{1x}^2 + v_{2x}^2 + \dots\dots\dots + v_{Nx}^2)$$

$$P = \frac{F_x}{L^2} = \frac{m}{L^3}\left(v_{1x}^2 + v_{2x}^2 + \dots\dots\dots + v_{Nx}^2\right) \text{------} (2)$$

Now as N is the total number of molecules each of mass m, so total mass of gas will be Nm. So the density of the gas will be:

$$Density = \frac{mass}{volume} \Longrightarrow \rho = \frac{Nm}{L^3} \Longrightarrow \frac{\rho}{N} = \frac{m}{L^3}$$

Equation (2) becomes:

$$P = \frac{\rho}{N}(v_{1x}^2 + v_{2x}^2 + \dots\dots\dots + v_{Nx}^2)$$

$$P = \rho\left(\frac{v_{1x}^2 + v_{2x}^2 + \dots\dots\dots + v_{Nx}^2}{N}\right)$$

The quantity within brackets is mean square velocity of gas molecules along x-axis and is denoted by $\overline{v_x^2}$. Therefore

$$P = \rho\ \overline{v_x^2}\ \text{-----------} (3)$$

For any molecule,

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

As the molecules have random motion. So, $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$

$$\overline{v^2} = \overline{v_x^2} + \overline{v_x^2} + \overline{v_x^2}$$

$$\overline{v^2} = 3\overline{v_x^2} \Longrightarrow \overline{v_x^2} = \frac{1}{3}\overline{v^2}$$

Equation (3) becomes:

$$P = \frac{1}{3}\rho\ \overline{v^2}\ \text{-------------} (4)$$

Root Mean Square Speed

From equation (4), we have

$$\overline{v^2} = \frac{3P}{\rho}$$

Taking square root on both sides

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3P}{\rho}}$$

$$v_{rms} = \sqrt{\frac{3P}{\rho}}$$

Dependence of Speed of Molecules on Temperature

As

$$Density\ of\ gas = \frac{mass}{volume} \quad \text{------------} \quad (5)$$

If M is the molar mass of the gas and n are the number of moles, then

$$Mass\ of\ gas = nM$$

Equation (5) will become:

$$\rho = \frac{nM}{V}$$

$$\Rightarrow V = \frac{nM}{\rho} \quad \text{------------} \quad (6)$$

From ideal gas law:

$$PV = nRT \Rightarrow V = \frac{nRT}{P} \quad \text{-----------} \quad (7)$$

Comparing equation (6) and (7), we get:

$$\frac{nM}{\rho} = \frac{nRT}{P}$$

$$\Rightarrow \frac{P}{\rho} = \frac{RT}{M}$$

$$\Rightarrow \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M}}$$

$$\Rightarrow v_{rms} = \sqrt{\frac{3RT}{M}}$$

If v_1 and v_2 are the speed of molecules of gas at temperature T_1 and T_2, then

$$v_1 = \sqrt{\frac{3RT_1}{M}} \text{ and } v_2 = \sqrt{\frac{3RT_2}{M}}$$

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

Kinetic Interpretation of Temperature

The pressure of ideal gas on the basis of kinetic theory of gas is given by the expression:

$$P = \frac{1}{3} \rho \, \overline{v^2}$$

Multiplying both sides by V, we get:

$$PV = \frac{1}{3} (\rho V) \, \overline{v^2} \quad \text{---------------} \quad (8)$$

Here $\rho V = mass \; of \; the \; gas$

If M is the molar mass of gas and n is the number of moles of gas, then

$$\rho V = nM, \text{ put in equation (8)}$$

$$PV = \frac{1}{3} nM \, \overline{v^2}$$

$$\Rightarrow nRT = \frac{1}{3} nM \, \overline{v^2}$$

$$\Rightarrow T = \frac{1}{3R} M \, \overline{v^2}$$

$$\Rightarrow T = \frac{2}{3R} \left(\frac{1}{2} M \, \overline{v^2} \right)$$

According to this equation, the average translational K.E per mole of an ideal gas is directly proportional to the absolute temperature of ideal gas.

$$\frac{1}{2} M \, \overline{v^2} = \frac{3}{2} RT$$

Dividing both sides by Avogadro number N_A

$$\Rightarrow \frac{1}{2} \frac{M \, \overline{v^2}}{N_A} = \frac{3}{2} \frac{RT}{N_A}$$

$$As \; M = nN_A \; and \; R = kN_A$$

$$\Rightarrow \frac{1}{2} \frac{nN_A \, \overline{v^2}}{N_A} = \frac{3}{2} \frac{kN_A T}{N_A}$$

$$\Rightarrow \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$$

$$\Rightarrow T = \frac{2}{3k} \left(\frac{1}{2} m \overline{v^2} \right)$$

This equation shows that temperature of gas is directly proportional to K.E per molecule.

Graham's Law of Diffusion

We know that temperature of gas is directly proportional to K.E per molecule i.e.,

$$T = \frac{2}{3k} \left(\frac{1}{2} m \overline{v^2} \right)$$

For two different gases at same temperature T and Pressure P, we can write as:

$$\frac{2}{3k}\left(\frac{1}{2}m_1\overline{v_1^2}\right) = \frac{2}{3k}\left(\frac{1}{2}m_2\overline{v_2^2}\right)$$

$$\Rightarrow m_1\overline{v_1^2} = m_2\overline{v_2^2}$$

$$\Rightarrow \frac{\overline{v_1^2}}{\overline{v_2^2}} = \frac{m_2}{m_1}$$

$$\Rightarrow \sqrt{\frac{\overline{v_1^2}}{\overline{v_2^2}}} = \sqrt{\frac{m_2}{m_1}}$$

$$\Rightarrow \frac{\overline{v_{1rms}}}{\overline{v_{2rms}}} = \sqrt{\frac{m_2}{m_1}}$$

According to this equation, the ratio of root mean square speeds of molecules of two different gases is equal to the inverse ratio of square root of their masses. This is known as Graham's law of diffusion.

Work Done on an Ideal Gas

Consider a gas contained in a cylinder having movable piston. We raise the temperature of gas, the gas expands and moves the piston up. The upward force exerted by the gas due to its pressure P is PA, where A is the area of the piston.

By Newton's 3rd law of motion, the piston exerts an equal and opposite force $-PA$ on the gas. So the work done on the gas is:

$$W = \int F \, dx$$

$$W = \int -PA \, dx \quad \text{------------} \quad (1)$$

Where dx is the displacement of the piston. In covering distance dx, the volume of the gas changes by $dV = Adx$.

So the equation (1) becomes:

$$W = -P \int dV$$

If the volume changes from V_i to V_f, then

$$W = -P \int_{V_i}^{V_f} dV$$

$$W = -P \left|V\right|_{V_i}^{V_f}$$

$$W = -P \left(V_f - V_i\right)$$

This equation shows that:

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- Work done on the gas during expansion is negative
- Work done on the gas during compression is positive.

Pressure Force is Non-Conservative

Consider an ideal gas undergo a change from initial condition (P_i , V_i) to the final condition (P_f , V_f). We take two different path between A and D i.e., path 1 (ABD) and path 2 (ACD).

Work Done along Path-ABD

Along the path ABD, first the pressure increases from P_i to P_f at constant volume V_i along AB and then volume increases from V_i to V_f at constant pressure P_f along BD. The total work done is equal to the area of rectangle BDEF (The area below line BD).
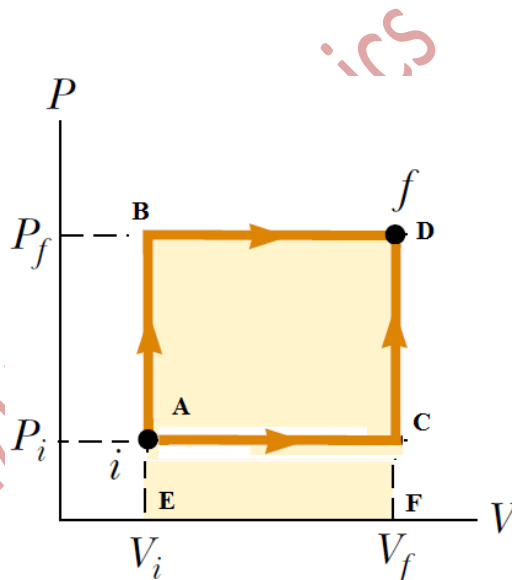
$$W_{ABD} = W_{AB} + W_{BD} \quad \text{----------- (1)}$$

- $W_{AB} = 0$, because $dV = 0$ i.e., volume is constant.

- $W_{BD} = \int_{V_i}^{V_f} -P_f dV = -P_f \int_{V_i}^{V_f} dV = -P_f |V|_{V_i}^{V_f} = -P_f (V_f - V_i)$

Equation (1) becomes:

$$W_{ABD} = W_{AB} + W_{BD} = 0 - P_f (V_f - V_i) = -P_f (V_f - V_i) \quad \text{---------- (2)}$$

Work Done along Path-ACD

Along the path ACD, first the volume increases from V_i to V_f at constant volume P_i along AC and then pressure increases from P_i to P_f at constant volume V_f along CD. The total work done is equal to the area of rectangle ACEF (The area below line AC)

$$W_{ACD} = W_{AC} + W_{CD} \quad \text{----------- (3)}$$

- $W_{CD} = 0$, because $dV = 0$ i.e., volume is constant.

- $W_{AC} = \int_{V_i}^{V_f} -P_i dV = -P_i \int_{V_i}^{V_f} dV = -P_i |V|_{V_i}^{V_f} = -P_i (V_f - V_i)$

Equation (3) becomes:

$$W_{ACD} = W_{AC} + W_{CD} = -P_i (V_f - V_i) - 0 = -P_i (V_f - V_i) \quad \text{----------- (4)}$$

Conclusion

From equation (2) and (4), it is clear:

$$W_{ABD} = W_{ACD}$$

So work done on the ideal gas along two different paths is different. Hence pressure force is non-conservative.

Work Done at Constant Volume

The work is zero in the process in which volume remains constant i.e., $dV = 0$ and hence $W = 0$ as shown along path AB and CD.

It should be noted that it is not sufficient that the process should start and end at the same volume. For the process ABDCA, the volume starts and ends at V_i but the work done is certainly not zero. The work is zero for vertical paths AB and DC, because the volume remains constant along these paths. The process in which volume remains constant is called isochoric process.
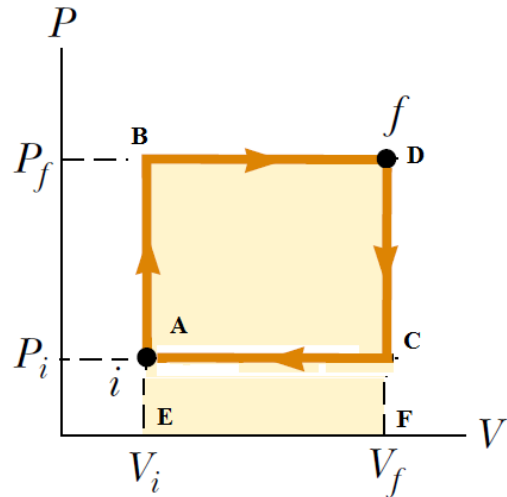
Work Done at Constant Pressure

The work done at constant pressure can be find out using expression:

$$W_{AC} = \int\limits_{V_i}^{V_f} -P_i dV = -P_i \int\limits_{V_i}^{V_f} dV = -P_i \left.|V|\right._{V_i}^{V_f} = -P_i \left(V_f - V_i\right)$$

Along the paths BD and CA, the work is being done at constant pressure.

- Work done on the gas is negative for path BD, because the volume increases along BD.
- Work done on the gas is positive for path CA, because the volume decreases along CA.

Work Done at Constant Temperature

The process in which temperature remains constant is called isothermal process. This process is represented in the PV diagram by hyperbolic curve as shown in the figure. This hyperbolic curve is called isotherm.
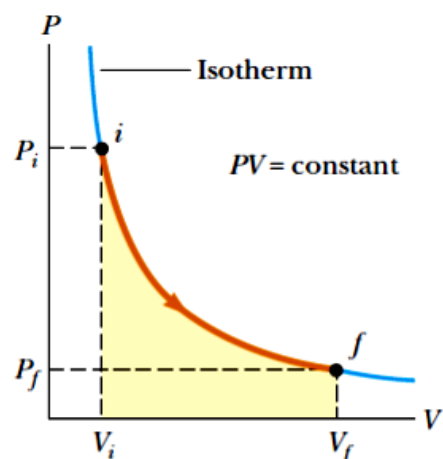
The work done in isothermal process is calculated by the equation:

$$W = \int_{V_i}^{V_f} -PdV$$

By the ideal gas equation:

$$PV = nRT \implies P = \frac{nRT}{V}$$

Therefore,

$$W = \int_{V_i}^{V_f} -\frac{nRT}{V} \, dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT |\ln V|_{V_i}^{V_f}$$

$$\Rightarrow W = -nRT(\ln V_f - \ln V_i)$$

$$\Rightarrow W = -nRT \ln \frac{V_f}{V_i}$$

Work Done at Thermal Isolation (Adiabatic Condition)

The process in which cylinder is completely insulated from its surrounding such that heat can't enter or leave the gas is called adiabatic process. The adiabatic process can be represented by the equation:

$PV^\gamma = K$ where K is a constant and $\gamma = \frac{c_P}{c_V}$.

On a PV diagram, this adiabatic process is represented by a hyperbolic curve (steeper than an isotherm), called adiabat.

The work done in adianatic process is calculated by the equation:

$$W = \int_{V_i}^{V_f} -P dV$$

As $P = \frac{K}{V^\gamma}$

Therefore,

$$W = \int_{V_i}^{V_f} -\frac{K}{V^\gamma} \, dV = -K \int_{V_i}^{V_f} \frac{dV}{V^\gamma} = -K \int_{V_i}^{V_f} V^{-\gamma} dV$$

$$\Rightarrow W = -K \left| \frac{V^{-\gamma+1}}{-\gamma+1} \right|_{V_i}^{V_f} = \frac{K}{\gamma-1} \left[V_f^{-\gamma+1} - V_i^{-\gamma+1} \right]$$

$$\Rightarrow W = \frac{1}{\gamma-1} \left[K V_f^{-\gamma+1} - K V_i^{-\gamma+1} \right]$$

Putting $K = P_i V_i{}^\gamma = P_f V_f{}^\gamma$

$$\Rightarrow W = \frac{1}{\gamma-1} \left[P_f V_f{}^\gamma V_f^{-\gamma+1} - P_i V_i{}^\gamma V_i^{-\gamma+1} \right]$$

$$\Rightarrow W = \frac{1}{\gamma-1} \left[P_f V_f - P_i V_i \right]$$

Using Ideal Gas Law: $PV = nRT$, we have

$$\Rightarrow W = \frac{1}{\gamma-1} \left[nRT_f - nRT_i \right]$$

$$\Rightarrow W = \frac{nR}{\gamma-1} \left[T_f - T_i \right]$$

This is the expression of work done during an adiabatic process.

The Internal Energy of an Ideal Gas

The sum of all forms of molecular energies of a substance is termed as its internal energy.

In the study of thermodynamics, usually the ideal gas is considered as working substance. The molecules of an ideal gas are mere point masses which have no force of attraction between them. So the internal energy of an ideal gas system is generally the translational K.E. The ideal gas has no internal energy due to vibrational and rotational motion.

Since the temperature of a system is defined as the average K.E of its molecules, thus for the ideal gas system, the internal energy is directly proportional to its temperature. It does not depends on pressure or volume of the gas. For the n moles of an ideal gas at temperature T, the internal energy of the ideal gas is written as:

$$E_{int} = n\left(\frac{1}{2}M\bar{v}^2\right) = \frac{3}{2}nRT$$

We can change the internal energy of the ideal gas by doing work on it. Suppose the ideal gas in cylinder is insulated from the surroundings and a work W is done on the gas. By law of conservation of energy:

$$\Delta E_{int} = \frac{3}{2}nR\Delta T$$

So the temperature changes are also positive.

Internal Energy of a Diatomic Gas

Let us consider a diatomic gas whose molecules have the shape of a dumbbell as shown in the figure. In this model, the center of mass of the molecule can translate in the x, y, and z directions (Fig. a). In addition, the molecule can rotate about three mutually perpendicular axes (Fig. b). We can neglect the rotation about the y axis because the molecule's moment of inertia I_y and its rotational energy $\frac{1}{2}I_y\omega^2$ about this axis are negligible compared with those associated with the x and z axes. Thus, there are five degrees of freedom for translation and rotation: three associated with the translational motion and two associated with the rotational motion:

$$(K.E)_{total} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_z\omega_z^2$$

According to theorem of equipartition of energy, the average energy of gas molecule per degree of freedom and
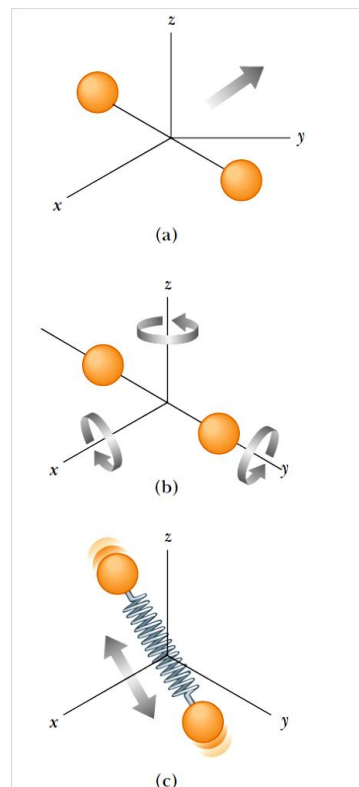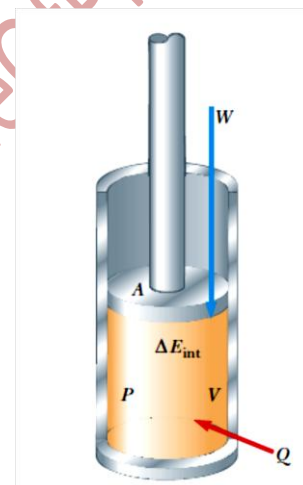
same and equal to $\frac{1}{2}k_B T$ where k_B is Boltzmann's constant and T is absolute temperature.

Because each degree of freedom contributes $\frac{1}{2}k_B T$ of energy per molecule, the internal energy for a system of N molecules, ignoring vibration for now, is

$$E_{int} = 3N\left(\frac{1}{2}k_B T\right) + 2N\left(\frac{1}{2}k_B T\right) = \frac{5}{2}Nk_B T = \frac{5}{2}nRT$$

The vibrational motion adds two more degrees of freedom, which correspond to the kinetic energy and the potential energy associated with vibrations along the length of the molecule. Hence, classical physics and the equipartition theorem in a model that includes all three types of motion predict a total internal energy of

$$E_{int} = 3N\left(\frac{1}{2}k_B T\right) + 2N\left(\frac{1}{2}k_B T\right) + 2N\left(\frac{1}{2}k_B T\right) = \frac{7}{2}Nk_B T = \frac{7}{2}nRT$$

The vibrational term in the internal energy is effective at high temperature. At low temperature, the vibrational and rotational motions can be frozen. So at low temperature, only three translational degrees of freedom are present. The experiments with gas molecule collision show that the internal energy of an atom is quantized.

The Vander Walls Equations of State

Kinetic theory of gases gives the microscopic description of behavior of ideal gas. But some of the assumptions of ideal gas are not true for real gases e.g., due to intermolecular forces the molecules have a small but non zero diameter which is against the assumption of the ideal gas model.

Moreover the range of intermolecular forces may be greater than the size of the molecule which is against our assumption that intermolecular forces are short range forces.

So the ideal gas equation needs modifications to account for the effect of finite size molecule and presence of intermolecular forces.

(i)   Effect of Finite Size of the Molecule

To consider the effect of finite size of molecule, we consider the molecule in the form of a hard sphere of diameter d. The distance between the centers of the two molecules can't be less than d.

Therefore, the free volume occupied by molecule is decreased by considering the finite size of molecule. If b is the decrease in volume due to molecules in one mole then decrease in volume due to molecules in n moles is equal to nb.

If V is the volume of container then the volume available to the gas is not V but $V - nb$. So the ideal gas equation takes the form:

$P(V - nb) = nRT$

$$P = \frac{nRT}{(V-nb)} \qquad \text{------------} \quad (1)$$

This shows that pressure of real gas is increased. Due to smaller volume, the molecules have more collisions and thus pressure is increased.

(ii)   Effect of Intermolecular Forces

To consider the effect of intermolecular forces, we take the range of intermolecular forces equal to diameter d of molecule. Let a single molecule is about to collide with the wall of container. This molecule also experiences attractive forces from other molecules lying within a distance d.

The sum of all intermolecular forces gives a resultant force on the molecule under consideration, which is directed away from the wall. So the molecule collides with the wall with a smaller force.

So due to intermolecular forces, the pressure is reduced. The decrease in pressure is proportional to the square of number of moles per unit volume $\left(\frac{n}{V}\right)^2$. The expression (1) becomes:

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

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

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

This is called the Vander Walls equation of state. The constant 'a' and 'b' can be determined experimentally and are called Vander Wall constants.