Explainations for the deviations:-

The following two postulates of the kinetic theory do not appear to hold good under all the conditions.

Postulate no. 1: The volume occupied by the molecules themselves is negligibly small as compared to the total volume occupied by the gas. This postulate can be justified only under ordinary conditions of temperature and pressure.

→ If the pressure becomes too high, the volume of gas decreases appreciably whereas the volume of the molecules will remain almost the same because the molecules are incompressible. Hence under conditions of high pressure, the volume occupied by the gas molecules will no longer be negligible in comparision with the volume of the gas.

→ when the temperature is lowered to a great extent. The total volume of the gas decreases considerably, but the volume occupied by the molecules themselves remains practically the same. In this case, the volume occupied by the molecules will no longer be negligible.

Hence Postulate 1 is not valid at high temperature and pressure.

Postulate no. 2:- The forces of attraction between gas molecules are negligible. This assumption is valid at low pressures or at high temperatures because under these conditions the molecules lie far apart from one another.

But at high pressures or at low temperatures, the volume is small and molecules lie closer to one another. The intermolecular forces of attraction are appreciable and cannot be ignored.

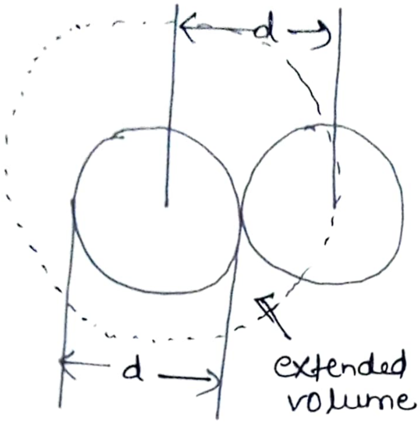
→ Thus Postulate 2 does not hold under conditions of high pressures and low temperature. It is neccessary to apply suitable corrections to the ideal gas equation so as to make it applicable to real gases.

Equations of state for Real (Imperfect) gas

A number of equations of state have been suggested to describe the P-V-T relationship in real gases. The two main correction terms can be introduced as:-

(1) Correction due to volume of gas molecules...

The ideal gas equation $PV = nRT$ is derived from the assumption that the gas molecules are mass point i.e. they do not have finite volume. Van der Waals abandoned this assumption and suggested that a correction nb should be subtracted from total volume V in order to get the ideal volume which is compressible.



In order to understand the meaning of correction term nb, it can be considered about two gas molecules as unpenetrable and incompressible spheres, each of which has diameter d.

As shown in the figure that the centres of the two spheres cannot approach each other a sphere of radius, d. For this pair of molecules, a sphere of radius d and volume $= \frac{4}{3}\pi d^3$ constitute what is known as <u>excluded volume</u>.

The excluded volume per molecule is half of the above volume, i.e. equal to $\frac{2}{3}\pi d^3$.
The actual volume of one gas molecule of radius r is $\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi d^3$.

$\therefore$ Excluded volume per molecule $= \frac{2}{3}\pi d^3$

$$= 4 \times \frac{1}{6}\pi d^3$$

$\Rightarrow$ 4 times the actual volume of the gas molecule.

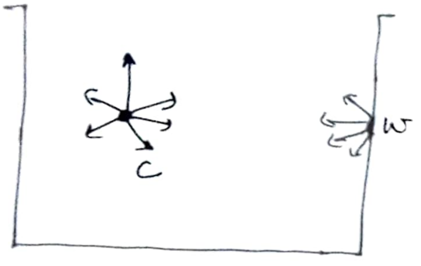
The excluded volume per mole of the gas would be $N_A \times 4 \times \frac{4}{3}\pi r^3 = b$, where N_A is the Avogadro's number.

The compressible volume per mole of gas would be V-b.

If volume V of the gas contains n moles, then the extended volume will be nb.

Hence ideal volume which is compressible would be V-nb. The volume b per mole is also known as co-volume.

2. Correction due to intermolecular forces of attraction :-



Molecular attraction

In the derivation of the ideal gas equation, it was assumed that there are no intermolecular forces of attraction. In real the case is different.

→ In the above image a molecule is lying somewhere in the mid of vessel at point C. It is being attracted uniformly at all sides by the neighboring molecules. These forces neutralize one another and there is no resultant attractive force on the molecules.

→ As the molecule approaches wall of container it experiences attractive forces from bulk of molecules behind it. It will strike the wall with lower velocity and hence exert lower pressure than it would have done with no force of attraction. Hence correction factor, p, is added to pressure to get ideal pressure.

Thus corrected pressure is (P+p).