

Reasons for deviation of real gases from Ideal Behavior:

In 1873, Vander walls, a Dutch Scientist tried to explain the reasons for deviation of real gases from ideal gas eqn. He modified the two assumptions in kinetic theory which are not exactly true. These assumptions are

- (a) the molecules are point-masses and thus molecules have definite masses but no volume.
- (b) There is no intermolecular attraction in the gases.

In fact, in a real gas, the volume of the bodies of the molecules may be quite appreciable even at ordinary Pr.

For example, at N.T.P, one gm-mole of a gas, i.e. 6.02×10^{23} molecules occupy a volume of 22400 cc.

The diameter of a molecule may be taken as of the order 2×10^{-8} cm. So, the space occupied by a molecule is

$$\frac{4}{3} \pi (2 \times 10^{-8})^3 = 3.3 \times 10^{-23} \text{ cc}$$

Hence, the space taken up by the molecules

$$= 6.02 \times 10^{23} \times 3.3 \times 10^{-23} = 20.46 \text{ cc}$$

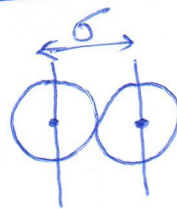
Thus at N.T.P the space occupied by the molecules themselves is nearly $\sim \frac{1}{1000}$ of the volume of the gas.

If the pr. be increased to say 10 atm, the volume of the gas would be approximately 2240 cc. Then, the fraction of this volume occupied by the molecule $= \frac{20.46}{2240} = \frac{1}{100}$, i.e. nearly one percent of the volume, which is no means negligible.

In the kinetic theory it has been presumed that no inter-molecular force exists and as such the collisions are perfectly elastic, the energy is all kinetic. But, in fact, there does exist a force of attraction between the molecules. On cooling, the gases are converted into liquids when the molecules ~~exhibit~~ exhibit appreciable cohesion. This indicates that a similar attraction exists between the molecules in the gas-phase also. Joule-Thomson's porous-plug experiment definitely proves the existence of intermolecular attraction of the gases.

Definite size of the gas molecules results from the repulsive forces acting on the gas molecules when they are approaching close to make collisions. When two molecules approach to each other, they cannot reach closer together beyond a certain distance σ , called the distance of closest approach and it is also called collision diameter.

Higher the intermolecular repulsion, greater is the value of σ



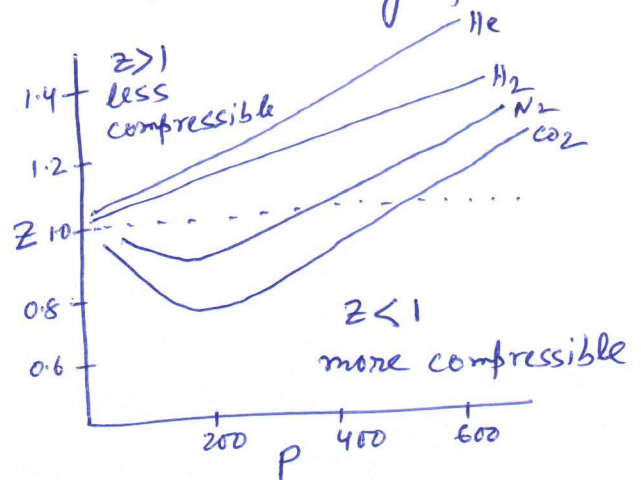
The Vander Waals radius $= \frac{\sigma}{2}$

Gas molecules have both attraction and repulsion among themselves. Thus, molecules initially attract each other as they approach and they repel each other when they collide. This happens due to the fact that attractive potential is long-range potential ($V_{\text{attraction}} \propto \frac{1}{r^6}$) while the repulsive potential is short-range ($V_{\text{repulsion}} \propto \frac{1}{r^{12}}$). r = Intermolecular distance betw. the molecules.

Qualitative explanation of Amagat's curves:

The concept of molecular attraction and repulsion can be used to explain the value of compressibility factor (z) qualitatively.

(i) At low P ($P \rightarrow 0$), the vol. of the gas is large, and intermolecular distance (r) is large, both attractive force and repulsive forces are negligibly small, so it can not affect the ideal behavior. z becomes one.



(ii) At high P , the r is small, the molecules are very close to each other. At this condition, short-range repulsive potential dominates over the long-range attractive potential. The gas becomes less compressible than ideal gas (where there is no intermolecular interaction) and $z > 1$.

(iii) At moderate P , the molecules are not very close and long-range attractive potential dominates over the short-range repulsive potential. The gas becomes more compressible and $z < 1$.

For H_2 and He gases, attractive potential is very small in comparison to repulsive potential so $z > 1$ always except when T is very low.

These intermolecular forces are popularly called van der Waals' forces and these are responsible for the deviation of real gases from ideal behavior.

Equation of states for Real Gases:

Many attempts have been made to modify the ideal gas equation and change it into a form which would represent P-V-T relations of real gases. corrections had to be introduced both for the pr. as well as the vol. and often two or more constants entered into the form. These equations are derived on empirical or semi-empirical basis. the forms of some of these equations are:

Van der waal's : $(P + \frac{a}{V^2})(V-b) = RT$

Dieterici : $P(V-b) = RT e^{\frac{-a}{RTV}}$

Berthelot : $(P + \frac{a}{TV^2})(V-b) = RT$

⋮

Kammerling onnes : $PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right)$

etc. etc.

Formulation of vander waal's Equation:

In 1873, Vander waal's modified the ideal gas eqn. for 1 mole : $P_{id} \bar{V}_{id} = RT$ by incorporating the size effect and intermolecular attraction effect of the real gases. These two effects are discussed under the vol. correction and pr. correction of the ideal gas Eqn.

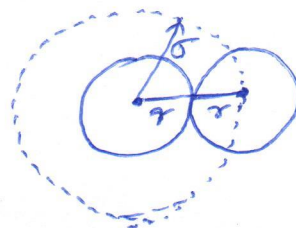
Volume correction:

In real gas, the molecules suffer strong repulsive force when they come close and collide with each other. This repulsive force gives rise to definite size of the gas molecules. They

have been assumed as rigid spheres. The available vol. for free movement of the molecules in real gas is less than \bar{V} . Let us take available space for free movement of 1 mole gas molecules; $\bar{V}_{id} = \bar{V} - b$, where \bar{V} is molar vol. of the gas and 'b' is vol. correction term due to definite size of the gas molecules. \bar{V}_{id} is the molar vol. of the ideal gas where gas molecules are regarded as point-masses.

Let us take σ is the collision diameter and r is the radius of each rigid sphere molecule. Thus,

$$\sigma = 2r$$



when two molecules encounter each other, the distance between the center of the two molecules would be σ . They can not approach beyond this distance. Thus, the sphere of radius σ will occupy a space unavailable for a pair of molecules.

Thus excluded vol. = $\frac{4}{3} \pi \sigma^3$ for a pair of molecules.

Thus effective vol. of a single molecule = $\frac{1}{2} \times \frac{4}{3} \pi \sigma^3 = \frac{2}{3} \pi \sigma^3$

and $b = \frac{2}{3} \pi N_A \sigma^3$, which is the effective vol. of Avogadro no. of molecules present in 1 mole gas.

$$\text{Thus, } b = \frac{2}{3} \pi N_A \sigma^3 = 4 \times \frac{4}{3} \pi N_A r^3$$

So, effective vol., b , is the four times the actual vol. of one mole gas molecules.

The vander waal's eqn. after vol. correction becomes,

$$P_{id} (\bar{V} - b) = RT$$

$$\begin{aligned} \text{Vol. of 1 mole of gas} &= 4 \times \frac{4}{3} \pi r^3 \times N_A \\ &= 4 \times \frac{4}{3} \times \frac{22}{7} \times (2 \times 10^{-8})^3 \times 6.023 \times 10^{23} \\ &\approx 10 \text{ cm}^3 \end{aligned}$$

$$1 \text{ mole gas in 100 cc beaker} = 100 \text{ cc}$$

$$\bar{V} = 100 - 10 \approx 90 \text{ cc}$$

Pressure Correction: -

Pressure of a gas is developed due to the wall-collisions of the gas molecules. Magnitude of pr. of a gas depends on both the frequency of molecular collisions with the walls and the force of each collision. The magnitude of both the factors is reduced by intermolecular attraction. Thus, pr. exerted by the molecules in the real gas (P) will be less than that if there had not been intermolecular attraction as in the ideal gas (P_{id}).

$$\text{Thus, } P_{id} > P \quad \text{or} \quad P_{id} = P + P_a$$

where, P_a is the pr. correction term, called internal pr. originating from attractive forces between the molecules. Higher the intermolecular attraction in a gas, greater is the magnitude of P_a . This reduction of pr. (P_a) acts with magnitude proportional to the density of the gas molecules. Both the frequency and force of each collisions are reduced by intermolecular attraction, so the pr. is reduced in proportion to square of the gas density. But density of gas is proportional to $\frac{1}{V}$. So, $P_a \propto \frac{1}{V^2}$; or $P_a = \frac{a}{V^2}$

$a = \text{const.}$ for the gas. Greater the intermolecular attraction of the gas, higher will be the value of 'a'. Thus, 'a' is a measure of intermolecular attraction of the gas. Incorporating both the vol. correction and pr. correction, the eqn. formed is called Vander wall's eqn. for 1 mole gas -

$$\left(P + \frac{a}{V^2} \right) (\bar{V} - b) = RT$$

To convert the eqn. for n moles, \bar{V} is to be replaced by V/n , where V is the vol. of n moles of the gas. Thus, Vander ~~wall~~ waals eqn. for n mole real gas:

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT; \quad \left| \begin{array}{l} \text{The reason for changing the vol. is} \\ \text{that it is an extensive property so it} \\ \text{is changed when the amount is changed.} \end{array} \right.$$

The gas which obeys Vander Waal's eqn. is called Vander waal's gas.