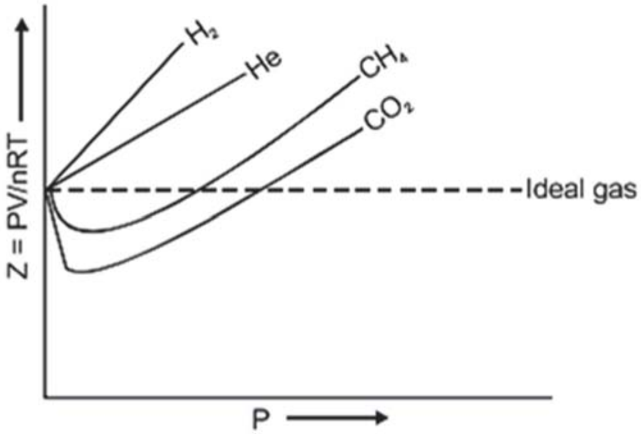
BEHAVIOR OF REAL GASES

The notion of an ideal gas is theoretical, as there is no actual gas that perfectly adheres to ideal behavior. Consequently, real gases, which exist in the practical realm, only approximately conform to the gas equation under two specific conditions:

(i) low pressure and

(ii) high temperature.

In order to assess the validity of the relationship described by the gas equation PV = nRT for real gases, a thorough examination of Boyle's Law was conducted through graphical representation for various gases such as CO, CH, He, and H_2. The plotted data of PV against P at constant temperature revealed deviations from ideal behavior across a spectrum of gases. Consequently, the conventional gas equation, PV = nRT, is not applicable to accurately describe the behavior of these gases. Therefore, an alternative equation becomes imperative to establish a correlation among pressure (P), volume (V), and temperature (T) for these real gases. This alternative, known as the van der Waals equation, takes the form $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$, where 'a' and 'b' represent the van der Waals constants. The van der Waals equation is designed to better accommodate deviations from ideal behavior, offering a more precise representation of the thermodynamic properties of non-ideal gases.



Causes of Deviation

The kinetic theory of gases introduces two theoretical assumptions, which, when adjusted, provide a more accurate representation of gases that deviate from ideal behavior:

(1) The first postulate posits that the volume of an individual gas molecule is negligible when compared to the overall volume of the gas. However, in reality, gas molecules do possess some volume, contributing to observed deviations from ideal behavior.

2. The second postulate suggests the absence of intermolecular forces of attraction between gaseous molecules. In reality, there exist either forces of attraction or repulsion among gaseous molecules, although these forces may be of a small magnitude.

By refining these two postulates, an equation emerges that is applicable to gases displaying deviations from ideal behavior. The extent of a gas's departure from ideal behavior can also be expressed in terms of the compressibility factor (Z),

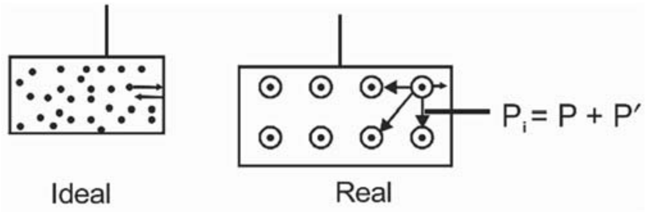
defined as: $Z = \frac{PV}{RT}$ [for 1 mole]

or $Z = \frac{(V_m)\text{real}}{(V_m)\text{ideal}}$ where, V_m represents the molar volume.

For an ideal gas, $Z = 1$.

In contrast, for a real gas, $Z > 1$ or $Z < 1$ indicating the degree of deviation from ideal behavior. This refined approach acknowledges the actual volume of gas molecules and the presence of intermolecular forces, offering a more comprehensive understanding of the behavior of real gases.

Pressure Correction



Where:
P represents the observed pressure of the gas.
P' denotes the pressure correction, accounting for pressure loss due to intermolecular forces of attraction and a decrease in the number of collisions on the wall.
The expression for P' is given by $P' \propto \frac{n^2}{v^2}$
and it can also be represented as $P' = a\left(\frac{n}{v}\right)^2$ where 'a' is the van der Waals constant.
The unit of 'a' is atm·liter^2·mol^{-2}.
Therefore, the corrected pressure, denoted as Pi, can be expressed as $Pi = (P + a\frac{n^2}{v^2})$,
which can be further simplified to $Pi = (P + \frac{a}{v_m^2})$ according to equation (i).
Here, v m represents the molar volume.
These equations provide a correction factor (P') to the observed pressure (P), considering the impact of intermolecular forces of attraction and the reduction in collision frequency on the wall. The inclusion of van der Waals constant 'a' facilitates a more accurate representation of the gas behavior, particularly when deviations from ideal behavior are observed.

Volume Correction

The ideal gas equation postulates that gas molecules are point masses, disregarding their actual volume. However, under high pressure conditions, it becomes evident that the volume of gas molecules cannot be overlooked in comparison to the volume of the container housing the gas. In response, a volume correction is introduced to account for this effect.
In the ideal gas equation, 'V' represents the volume of the container in which gas molecules move freely. Yet, since gas molecules themselves occupy space, their movement is now confined to the adjusted volume (V – nb), where 'nb' corresponds to the incompressible volume attributed to the impenetrable nature of gas molecules.
This volume correction is expressed as:

$$C_{\text{corrected}} = V - nb \qquad \text{(equation ii)}$$

Here, 'b' signifies the van der Waals constant, and 'n' represents the number of moles of the gas. This correction takes into account the volume occupied by the gas molecules, acknowledging their impenetrable nature as spheres, thus refining the ideal gas equation to better suit real-world conditions, particularly at elevated pressures.

van der Waal's Equation

Expressed by the ideal gas equation as:

$$P_{\text{ideal}} \cdot V_{\text{ideal}} = nRT_{\text{ideal}} \qquad \text{(equation iii).}$$

where P_{ideal} is the ideal pressure, V_{ideal} is the ideal volume, n represents the number of moles, and R is the ideal gas constant.

By substituting the values of P_{ideal} and V_{ideal} from equation (i) and equation (ii) into equation (iii).
we arrive at the van der Waals equation, which is a more comprehensive representation for real gases:

$$P + \frac{an^2}{V^2}(V - nb) = nRT$$

In this van der Waals equation:

- P signifies the observed pressure of the gas.
- V represents the volume of the gas.
- n is the number of moles of the gas.
- T is the temperature.
- a and b are the van der Waals constants.

This modified equation takes into consideration the volume correction $(V - nb)$ and the pressure correction term $(\frac{an^2}{V^2})$, offering a more accurate representation of the behavior of real gases, especially under conditions where deviations from ideal behavior are notable.

Magnitude of 'b'

The volume of a sphere with dotted markings is calculated using the formula $\frac{4}{3}\pi(2r)^3$,

which simplifies to $8 \times \frac{4}{3}\pi r^3$.

If we consider a single molecule, the volume occupied by it is $4 \times \frac{4}{3}\pi r^3$.

Now, if we extend this to N_A molecules (where N_A is Avogadro's number), the excluded volume b is expressed as $4 \times \frac{4}{3}\pi r^3 N_A$, or more conveniently $b = 4V_m$,

where V_m represents the volume occupied by one mole of molecules (and not the volume of the container).

In essence, the excluded volume is four times the actual volume occupied by a single molecule. This calculation helps in understanding the spatial requirements of molecules within a given volume, considering both individual and collective scenarios.