Question #61120, Chemistry / Physical Chemistry | completed

Task:

Derive van der Waals equation.

Answer:

For ideal gas, equation is true: $PV_{perfect} = nRT$

For real gas:

Volume correction:

The volume available for the gas molecules is less than the volume of the container, V. The available volume is obtained by subtracting excluded volume of ‘n’ moles of gas, nb from the volume of the container. Available volume = V - nb. Where 'b' is a constant characteristic of a gas. The ideal gas equation can be written after correcting for this as: $P(V - nb) = nRT$.

Pressure correction:

The pressure of the real gas is less than the expected pressure due to attractions between the molecules. These attractions slow down the motion of gas molecules and result in:

1) reduction of frequency of collissions over the walls and

2) reduction in the force with which the molecules strike the walls.

Hence: $P_{ideal} = P_{real} + p$

Where p = reduction in pressure

However the reduction in pressure is proportional to the square of molar concentration, n/V.

$$\text{The reduction in pressure (p)} \propto \frac{n}{V} \text{x} \frac{n}{V}$$

One factor for reduction in frequency of collisions and the second factor for reduction in strength of their impulses on the walls. Or

$$\text{Reduction in pressure (p)} = a\left(\frac{n}{V}\right)^2$$

where 'a' is a proportionality constant characteristic of a gas. Therefore:

$$P_{ideal} = P_{real} + \text{p} = \left(P + a\frac{n^2}{V^2}\right)$$

This is known as van der Waals equation of state. For one mole of a gas, the equation can be written as:

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

Where V_m = volume occupied by one mole of a real gas.