

## Limitations of Vander Waal's equation, and equations of state regarding behaviour of real gases.

The Vander Waal's equation is successful to explain the P-V-T behaviour of real gases at high temperature and low pressure. However, when the values of  $a$  and  $b$  are substituted in Vander Waal's equation the P-V-T relationship shows a appreciable deviation when pressure is too high or the temperature is too low.

This is so, because the values of  $a$  and  $b$  vary with temperature.

Several other equations of state have been proposed to express the P-V-T behaviour of real gases.

Some important equations of state are given below.

### (a) Berthelot Equation: -

The Berthelot Equation may be represented as

$$P = \frac{RT}{V-b} - \frac{a}{TV^2}$$

Here  $b$  has the same significance as in the Vander Waal's equation, but  $a$  has the dimension of Temperature.

This is particularly more accurate than Vander Waal's equation when used to calculate molecular masses of gases.

### (b) Dieterici equation: -

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

The above Dieterici equation gives more satisfactory results at high pressure than the Vander Waal's equation.

Dieterici made allowance in his equation for the effect of inter molecular attraction on the pressure by incorporating the term  $e^{-\frac{a}{RTV}}$ .

### (c) Clausius Equation: -

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

where  $c$  is the new constant. This equation is fairly satisfactory but does not hold for all the gases.

### (d) Virial Equation: - Virial equation may be represented as

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots$$

This equation was developed by Kammerlingh and Onnes. The virial (meaning force) equation is in terms of volume for one mole of a gas.

In terms of pressure, the equation is

$$PV = RT + BP + CP^2 + DP^3 + \dots$$