

Vander Waal's equation.

(1) To rectify the errors caused by ignoring the intermolecular forces of attraction and the volume occupied by molecules, Vander Waal (in 1873) modified the ideal gas equation by introducing two corrections,

- (i) Volume correction
- (ii) Pressure correction

(2) Vander Waal's equation is obeyed by the real gases over wide range of temperatures and pressures, hence it is called equation of state for the real gases.

(3) The Vander Waal's equation for n moles of the gas is,

$$\left(P + \frac{n^2 a}{V^2} \right) [V - nb] = nRT$$

Pressure correction for molecular attraction Volume correction for finite size of molecules

a and b are Vander Waal's constants whose values depend on the nature of the gas. Normally for a gas $a \gg b$.

- (i) **Constant a:** It is an indirect measure of magnitude of attractive forces between the molecules. Greater is the value of a, more easily the gas can be liquefied. Thus the easily liquefiable gases (like $SO_2 > NH_3 > H_2S > CO_2$) have high values than the permanent gases (like $N_2 > O_2 > H_2 > He$).

Units of 'a' are: $\text{atm. L}^2 \text{ mol}^{-2}$ or $\text{atm. m}^6 \text{ mol}^{-2}$ or $\text{Nm}^4 \text{ mol}^{-2}$ (S.I. unit).

- (ii) **Constant b:** Also called co-volume or excluded volume,

$$b = 4 N_0 v \left(= \frac{4}{3} \pi r^3 \right)$$

Its value gives an idea about the effective size of gas molecules. Greater is the value of b, larger is the size and smaller is the compressible volume. As b is the effective volume of the gas molecules, the constant value of b for any gas over a wide range of temperature and pressure indicates that the gas molecules are incompressible.

Units of 'b' are: L mol^{-1} or $\text{m}^3 \text{ mol}^{-1}$ (S.I. unit)

- (iii) Vander Waal's constant for some gases are,

Name of gas	a		b	
	atm litre ² mol ⁻²	Nm ⁴ mol ⁻²	litre mol ⁻¹	m ³ mol ⁻¹
Hydrogen	0.245	0.0266	0.0266	0.0266
Oxygen	1.360	0.1378	0.0318	0.0318
Nitrogen	1.390	0.1408	0.039	0.0391
Chlorine	6.493	0.6577	0.0562	0.0562
Carbon dioxide	3.590	0.3637	0.0428	0.0428
Ammonia	4.170	0.4210	0.0371	0.0371
Sulphur dioxide	6.170	0.678	0.0564	0.0564
Methane	2.253		0.0428	

(iv) The two Vander Waal's constants and Boyle's temperature (T_B) are related as,

$$T_B = \frac{a}{bR}$$

(4) **Vander Waal's equation at different temperature and pressures:**

(i) **When pressure is extremely low:** For one mole of gas,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ or } PV = RT - \frac{a}{V} + Pb + \frac{ab}{V^2}$$

(ii) **When pressure is extremely high:** For one mole of gas,

$$PV = RT + Pb; \frac{PV}{RT} = 1 + \frac{Pb}{RT} \text{ or } Z = 1 + \frac{Pb}{RT}$$

Where Z is compressibility factor.

(iii) **When temperature is extremely high:** For one mole of gas,

$$PV = RT .$$

(iv) **When pressure is low:** For one mole of gas,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ or } PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \text{ or } \frac{PV}{RT} = 1 - \frac{a}{VRT} \text{ or } Z = 1 - \frac{a}{VRT}$$

(v) **For hydrogen:** Molecular mass of hydrogen is small hence value of 'a' will be small owing to smaller intermolecular force. Thus the terms $\frac{a}{V}$ and $\frac{ab}{V^2}$ may be ignored.

Then Vander Waal's equation becomes,

$$PV = RT + Pb \text{ or } \frac{PV}{RT} = 1 + \frac{Pb}{RT} \text{ or } Z = 1 + \frac{Pb}{RT}$$

In case of hydrogen, compressibility factor is always greater than one.

(5) **Merits of Vander Waal's equation:**

(i) The Vander Waal's equation holds good for real gases up to moderately high pressures.

(ii) The equation represents the trend of the isotherms representing the variation of PV with P for various gases.

(iii) From the Vander Waal's equation it is possible to obtain expressions of Boyle's temperature, critical constants and inversion temperature in terms of the Vander Waal's constants 'a' and 'b'.

(iv) Vander Waal's equation is useful in obtaining a 'reduced equation of state' which being a general equation of state has the advantage that a single curve can be obtained for all gases when the equation is graphically represented by plotting the variables.

(6) **Limitations of Vander Waal's equation:**

(i) This equation shows appreciable deviations at too low temperatures or too high pressures.

(ii) The values of Vander Waal's constants a and b do not remain constant over the entire ranges of T and P, hence this equation is valid only over specific range of T and P.

(7) **Other equations of state:** In addition to Vander Waal's equation, there are also equations of state which have been used to explain real behavior of gases are,

(i) **Clausius equation:** $\left[P + \frac{a}{T(V+c)^2} \right] (V-b) = RT$. Here 'c' is another constant besides a, b and R.

(ii) **Berthelot equation:** $\left(P + \frac{a}{TV^2} \right) (V-b) = RT$.

(iii) **Wohl equation:**
$$P = \frac{RT}{(V-b)} - \frac{a}{V(V-b)} + \frac{c}{V^2}$$

(iv) **Dieterici equation:**
$$P = \frac{RT}{V-b} \cdot e^{-a/RTV}$$
. The expression is derived on the basis of the concept that molecules near the wall will have higher potential energy than those in the bulk.

(v) **Kammerlingh Onnes equation:** It is the most general or satisfactory expression as equation expresses PV as a power series of P at a given temperature.

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

Here coefficients A, B, C etc. are known as first, second and third etc. virial coefficients.

(a) Virial coefficients are different for different gases.

(b) At very low pressure, first virial coefficient, $A = RT$.

(c) At high pressure, other virial coefficients also become important and must be considered.