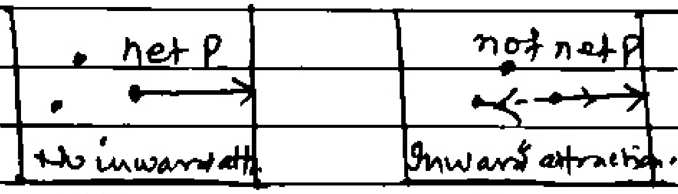
Vanderwaal equation OR Real gas equation:-

Ideal gas follow Boyle's law, Charle's law & Avogadro's law or we can say it follow ideal gas equation i.e PV = nRT at all temperature and pressure, but the real gas do not follow ideal gas equation at all the range of temperature and pressure. Even according to kinetic theory of gas two points are valid only for ideal gas it do not followed by real gas, that two points are as follows:

1) There is no force of attraction among the molecule themself.
11) The volume of one molecule is negligible with respect to entire volume of gas.

When there is no force of attraction among the molecule in ideal gas, then it can give net pressure on wall during collision. & the volume of one molecule is negligible with respect to entire volume ~~but~~ the same is not valid for real gas. So Vanderwaal concluded if the pressure and volume these two parameters are corrected in ideal gas equation then it can ~~behave~~ be applicable for real gas also. He made such an equation by correcting pressure ~~and volume of ideal~~ gas equation which has receeved the name Vanderwaal equation which is also called Real gas equation.

Correction in pressure



Ideal gas Real gas.

As we know from ideal gas equation $PV = nRT$ it is only for ideal gas not for real gas. Kinetic theory of gas says there is no force of attraction among the gaseous molecule but reals gas have. A real gas can behave as ideal gas only when temperature is high (that minimum temperature above which a real gas behave as ideal gas is called Boyle's temp). and pressure is low. In this condition volume of gas increases with same amount of gas so the distance between molecule increase(Max) hence force of attraction becomes minimum, and just reverse when pressure is high & temperature is low then volume decreases with same amount of gas so distance of molecule decreases and in the mean time force of attraction occurs among the molecule, So a molecule which is going to collide with wall experience an inward force of attraction hence it can not exert net pressure on wall, or the pressure applied on the wall is lesser than the molecule of ideal gas so ~~there~~ there should be some addition in the pressure exerted by the molecule of real gas by which it ~~should~~ will be equal to the pressure of ideal gas molecule, That's why need in correction of pressure was required. The correction in pressure

$$P_{Total} = P_{wall} + P_{external \text{ or inside attraction}}$$

$$P_T = P_w + P_i \quad \text{———— I}$$

Pressure on the wall of container + Pressure due to inside molecule's addition is equal to the pressure of total.

Pressure from the inside molecule depends on 1) Collision frequency ii) force of each collision. these two terms together called force of attractive force which is directly proportional to the square of molar concentration $(\frac{n}{V})$.

$$P_i \propto \left(\frac{n}{V}\right)^2$$

$$P_i \propto \frac{n^2}{V^2} \quad \text{———— II}$$

$$P_i = a \cdot \frac{n^2}{V^2}$$ — II where a is a ~~constant~~ constant called Vanderwaal constant.

Now we put the value of P_I from eqn II to Equation I we have:

$$P_T = P + \frac{an^2}{V^2} \quad \text{— III}$$

In ideal gas equation $P = P_T$, so, instead of P we will write in real gas eqn $P + \frac{an^2}{V^2}$.

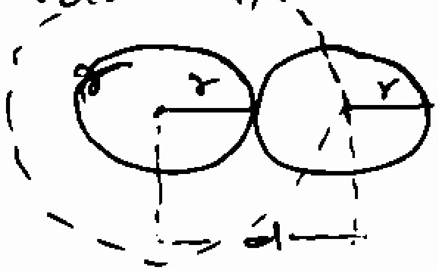
Correction in Volume :→ suppose n moles of gas is contained in container having volume V. When the volume occupied by the molecules are negligible with respect to entire volume of the gas, then two volumes are there i) volume occupied by the molecule (b) ii) free volume where molecule can move freely.

Actual volume available for free movement of molecule = $V - b$
where V = total volume,
b = volume of molecules, here b is a constant called Vanderwaal constant, which represent the size of molecule. In container the no of moles is n so
Volume available for free movement = $V - nb$ — IV
In ideal gas equation volume 'V' represent to available volume in container for free movement.

The excluded volume is generally treated as constant & characteristics of each gas.

Teacher's Signature : ____________

It can be proved that excluded volume is not equal to total volume of actual volume but it is four times the actual volume of gas.



Dotted line sphere in given figure above having diameter 'd' will not be available for the pair of molecule

The excluded volume for the pair of molecule =

$$V_{pair} = \frac{4}{3}\pi d^3 \quad (\because \text{Volume of sphere} = \tfrac{4}{3}\pi r^3)$$

$$= \frac{4}{3}\pi \cdot (2r)^3$$

$$= 8\left(\frac{4}{3}\cdot \pi r^3\right)$$

hence excluded volume per molecule:

$$= \frac{1}{2}\times 8\left(\frac{4}{3}\pi r^3\right)$$

$$= 4\times\left(\frac{4}{3}\pi r^3\right)$$

$$= 4V_m$$

Here $V_i = 4V_m$

V_i = Ecluded volume per molecule.

V_m = volume of the single gas molecule

Now when we put the Corrected P & V value in ideal gas equation Then a new equation is obtained Called Vanderwaal equation or real gas equation. i.e

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT. \quad \text{— } \underline{V}$$

Equation V is Vanderwaal equation or real gas equation.

Wher a & b are Constant Called Vanderwaal Constants.

Significance of Vanderwaal Constant:

1) First Vanderwaal Constant is 'a' ~~which~~

a) It is the measure of force of attraction of molecules among themselves.

b) Larger the value of a means gas can be liquid easily.

'a' $\propto$ liquifaction of gas.

value of a for different gas

$SO_2 > NH_3 > HCl > CO_2 > N_2 > O_2 > H_2 > He$.

ii) Second Vanderwaal Constant is 'b'. It represent

a) Size of molecules, mean lesser value of 'b' will take less volume, more value of b means large volume.

iii. Value of b $\propto \frac{1}{\text{Compressibility}}$

Unit of 'a' & 'b'.

$$P = \frac{an^2}{V^2}$$

$$a = \frac{PV^2}{n^2} = \frac{atm \times lit^2}{(mol)^2} = atm.lit^2.mol^{-2}$$

again $V_i = V - nb$

$$b = \frac{V - V_i}{n} = \frac{Volume}{Mol}, \; lit\,mol^{-1}.$$

Limitation of vanderwaal ~~constant~~ equation :- Vander-wall equation fails if the pressure of the gas is high and the temperature is near critical temperature.

Usefulness: vanderwaal equation can be applied for real gases at wide range of temperature & pressure.