* Difference between Real and Ideal gas

Real and Ideal gas → An ideal perfect gas is that which is strictly obeys gas laws i.e Boyle's law and charle's law as well as gas equation $PV = RT$.

All real gases show some deviation from gas laws particularly at low temperatu and high pressures. At very low pressures, the forces of intermolecular attraction are negligible. Therefore, at low pressure, a real gas also obeys the gas equation $PV = RT$.

An ideal gas can thus be defined as a real gas at low pressure. The internal energy of an ideal gas is a function of temperature only but for a real gas internal energy is a function of pressure and temperature.

* Limitations of Vander Waals equation

① It does not tell us when the condensation begins.

② The values of a and b do not remain constant at all temperatures

③ If we calculate the values of critical constants, we find that $\frac{RT_c}{P_cV_c} = \frac{8}{3}$ for all gases, but actually the value of $\frac{RT_c}{P_cV_c}$ varies with the gas and has an average values of 3.77.

④ Also the critical volume $V_c = 3b$ theoretically, though experimentally it is equal to 2b.

Ideal gas or Perfect gas

An ideal gas is one which strictly obeys Boyle's law and Charle's law under all conditions of temperature and pressure. Gases are less compressible and forces of intermolecular attractions are less significant. The internal energy is wholly kinetic depending on the temperature only.

Deviation from gas laws

It is found that no real gas strictly obeys the gas laws. Gases which are easily liquefied such as CO_2, ammonia etc, show marked deviation from gas laws. The so called permanent gases such as oxygen, Nitrogen, Hydrogen etc, show little deviation at ordinary temperatures and pressures but marked deviation at low temperatures and high pressures. In case of real gas, internal energy depends upon pressure and temperature.

Boyle temperature (TB) – The temperature below which gases are highly compressible and this suggests the existence of intermolecular attractions and beyond this temperature, Boyle's law is obeyed and intermolecular attractions are less ~~de~~ significant.

Critical temperature (Tc) – The temperature below which the gas can be liquefied by the application of pressure alone and above this temperature the gas can not be liquefied howsoever large the applied pressure may be.

Critical pressure (Pc) – The pressure applied to ~~g~~ the gas at its critical temperature so that it gets liquefied.

Critical volume (Vc) – It is the particular volume of a gas at critical temperature and critical pressure.

Critical Constants – The critical temperature and the corresponding values of pressure and volume at the critical point are called the critical constants.

At the critical point, the rate of change of pressure with volume i.e $\frac{dp}{dv} = 0$. This point is called the point of inflexion.

According to Vander Waals equation,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{——} ①$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{——} ②$$

Diff P w.r.t V,

$$\frac{dP}{dV} = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} \quad \text{——} ③$$

At the critical point

$$\frac{dP}{dV} = 0$$

$$T = T_c$$

$$V = V_c$$

$$\therefore \frac{-RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0$$ ~~—— ④~~

$$\frac{2a}{V_c^3} = \frac{RT_c}{(V_c-b)^2} \quad \text{——} ④$$

Diff equation ③ w.r.t V.

$$\frac{d^2P}{dV^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

At the critical point

$$\frac{d^2P}{dV^2} = 0$$

$$T = T_c$$

$$V = V_c$$

$$\therefore \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0$$

$$\frac{6a}{V_c^4} = \frac{2RT_c}{(V_c-b)^3} \quad \text{——} ⑤$$

Dividing ④ by ⑤

$$\frac{V_c}{3} = \frac{V_c - b}{2}$$

$$2V_c = 3V_c - 3b$$

$$V_c = 3b \quad \text{——} ⑥$$

Substituting the value of $V_c = 3b$ in eqn ④

$$\frac{2a}{27b^3} = \frac{RT_c}{4b^2}$$

$$\boxed{T_c = \frac{8a}{27Rb}} \quad \text{———} ⑦$$

Substituting these values of V_c and T_c in equation ②

$$P_c = \frac{R \times 8a}{27Rb(2b)} - \frac{a}{9b^2}$$

$$\boxed{P_c = \frac{a}{27b^2}}$$

Coefficients of Vander Waals Constants

$$V_c = 3b \quad \text{———} (i)$$

$$P_c = \frac{a}{27b^2} \quad \text{———} (ii)$$

$$T_c = \frac{8a}{27Rb} \quad \text{———} (iii)$$

$$\frac{T_c^2}{P_c} = \frac{64a^2}{(27)^2R^2b^2} \times \frac{27b^2}{a}$$

$$= \frac{64a}{27R^2}$$

$$\boxed{a = \frac{27}{64}\frac{R^2T_c^2}{P_c}}$$

Dividing (iii) by (ii)

$$\frac{T_c}{P_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a}$$ ✓

$$= \frac{8b}{R}$$

$$\boxed{b = \frac{RT_c}{8P_c}}$$

Also

✓ $$\frac{RT_c}{P_cV_c} = \frac{R(8a)}{27Rb} \cdot \frac{27b^2}{a \cdot 3b}$$

$$= 8/3$$

✓ Critical Coefficient of a gas.