Critical phenomenon - Critical constants of gas -

A gas can maintain their existance when temperature and pressure is accordingly. At high temperature and low pressure the a real gas can behave as ideal gas. Just opposite to this Condition at low temperature and high pressure a gas can be liquifeed. As temperature decreases the kinetic energy of the molecule decreases motion of molecule decreases, volume decreases at a high pressure gas converts into liquid. Hence to liquify the gas there are Two parameters first is temperature (low) & second is pressure (high).

As we encrease the temperature gradually then a time comes when whatever high pressure we apply on gas it can not be liquifeed, this minimum temperature at & above which gas can not be liquifeed even by applying a high pressure is Called Critical ~~p~~ temperature (Tc). Similarly that minimum pressure required at which we can liquify the gas at Critical temperature is called Critical pressure (Pc). The volume of one mole of gas at Critical Temperature & Critical pressure is called Critical Volume (Vc).

Critical Parameters	Symbolic representation
Critical temperature	T_c
Critical Pressure	P_c
Critical Volume	V_c

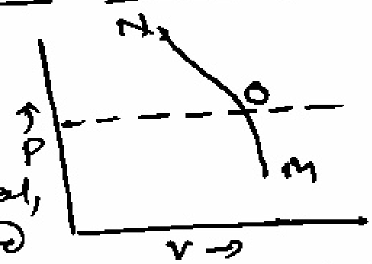
<u>For example</u>: The T_c, P_c & V_c value of CO_2.

for CO_2 $\quad T_c = 30.98^{\circ C} = 304.13 K$

$$P_c = 73.9 \text{ atm.}$$

$$V_c = 95.6 \text{ cm}^3 \text{ mol}^{-1}$$

<u>Relation between Critical Constants & Vander-waal Constants</u>: →



At a Critical Isotherm MON, the Critical point 'O' curve is horizontal, so the the value of $\frac{dp}{dv} = 0$. and ~~and~~ at this point the Tangent at such a point is said to stationary, So $\frac{d^2p}{dv^2} = 0$.

By vanderwaal equation for 1 mole of gas.

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

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

Defferential equation I we have

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

Now differentiate equation II we have.

$$\frac{d^2p}{dv^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \text{ —— } \overline{III}$$

At Critical point, $T = T_c$, $P = P_c$, $V = V_c$ then equation I can be written as:-
Here $dp/dv = 0$, $d^2P/dv^2 = 0$.

$$P_c = \frac{RT_c}{(V_c - b)} - \frac{a}{V_c^2} \text{ —— } \overline{IV}$$

- from eqn II we have

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

$$\text{So, } \frac{2a}{V_c^3} = \frac{RT_c}{(V_c-b)^2} \text{ —— } \overline{V}$$

From eqn III

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

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

Devide Eqn V by VI we have.

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

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

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or $\frac{\cancel{2}a}{\cancel{V_c^3}} \times \frac{\overset{V_c}{\cancel{V_c^4}}}{\underset{3}{\cancel{6}}a} = \frac{\cancel{RT_c}}{\cancel{(V_c-b)^2}} \times \frac{\overset{(V_c-b)}{\cancel{(V_c-b)^3}}}{2\cancel{R}T}$

or $\frac{V_c}{3} = \frac{(V_c-b)}{2}$

or $2V_c = 3V_c - 3b$

or $3V_c - 2V_c = 3b$

or $\boxed{V_c = 3b}$ ——— VII

Substitute equation VII to V we have:

$\frac{2a}{(3b)^3} = \frac{RT_c}{(3b-b)^2}$

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

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

$= \frac{8a}{27b} = RT_c$

or $\boxed{T_c = \frac{8a}{27bR}}$ ——— VIII

[redacted]

~~R~~-II

Now we put the value of Vc (from vii) & Tc (from eqn viii) in the ~~above~~ equation(1) we have.

$$P_c = \frac{\cancel{R} \times \frac{8a}{27b\cancel{R}}}{(3b-b)} - \frac{a}{(3b)^2}$$

$$\text{or } P_c = \frac{\frac{8a}{27b}}{2b} - \frac{a}{9b^2}$$

$$\text{or } P_c = \frac{8a}{54b^2} - \frac{a}{9b^2}$$

$$\text{or } P_c = \frac{8a - 6a}{54b^2}$$

$$\text{or } P_c = \frac{\cancel{2}a}{\cancel{54}_{27} b^2}$$

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

Hence

$$\boxed{\begin{aligned} V_c &= 3b \\ T_c &= \frac{8a}{27bR} \\ P_c &= \frac{a}{27b^2} \end{aligned}}$$

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