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B.Sc (Part-1) Hons
Paper-II

Critical constants of a gas in terms of the constants a and b of the vander walls equation.

The critical constant of a gas are:- critical temperature, critical pressure and critical volume.

Critical temperature:— The critical temperature of a gas is the highest temperature at which the gas can be liquefied by pressure, but above which no liquefaction is possible, however great the pressure.

Critical pressure:— The pressure required to liquefy a gas at its critical temprature is called the critical pressure.

Critical volume:— The volume occupied by 1 gram of the gas at the critical temperature and the criticle pressure is called the critical volume.

The vander walls equation can be written in the fallowing form

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

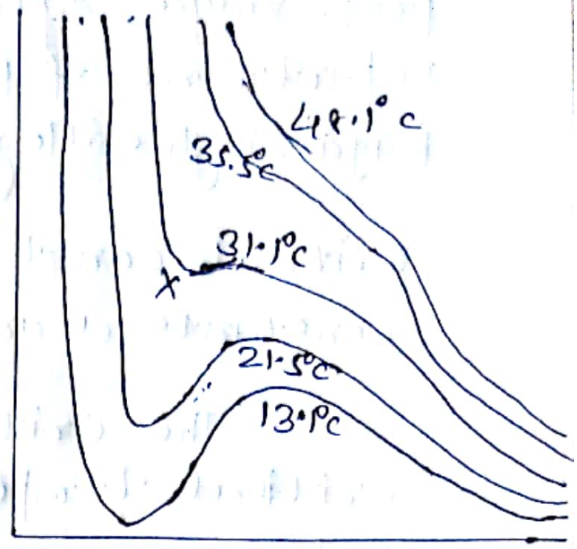
If P is plotted against V at different constant values of T, a set of isothermals is obtained in figure. The isothermal through the critical point X is horizontal at X i.e. the slope of the isothermal at X is zero. Therefore at X

$$\left(\frac{dP}{dV}\right)_T = 0$$

Also the curvatures of this isothermal on the two sides of the critical point X are opposite i.e. the point X is a point of inflection.

Therefore at X

$$\left(\frac{d^2p}{dV^2}\right)_T = 0$$



Applying these two conditions to the vanderwalls equation ①

we get $\left(\frac{dp}{dT}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0$ ——— ②

and $\left(\frac{d^2p}{dV^2}\right)_T = \frac{2RT}{(V-b)^3} + \frac{6a}{V^4} = 0$ ——— ③

But, the critical point $p = P_c$, $V = V_c$ and $T = T_c$ Hence

from equation ① $P_c = \frac{RT}{(V_c-b)} - \frac{a}{V_c^2}$ ——— ④

from ② $\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3}$ ——— ⑤

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

Dividing equation (10) by (11) we get

$\frac{1}{2}(V_c - b) = \frac{1}{3}V_c$

or, $V_c = 3b$ ——— (7)

Substituting $V_c = 3b$ in equation (5), we get

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

$\therefore T_c = \frac{8a}{27bR}$ ——— ⑧

Substituting $V_c = 3b$ and $T_c = \frac{8a}{27bR}$ in eqn (4)

$P_c = \frac{R}{2b}\left(\frac{8a}{27bR}\right) - \frac{a}{9b^2}$, or, $P_c = \frac{a}{27b^2}$ ——— (9)

$\therefore \frac{RT_c}{P_cV_c} = \frac{R\,8a}{27bR}\left(\frac{27b^2}{a}\right)\cdot\frac{1}{3b} = \frac{8}{3} = 2.67$

$\frac{RT_c}{P_cV_c}$ is called the 'Critical coefficient' and is the same for all gases.