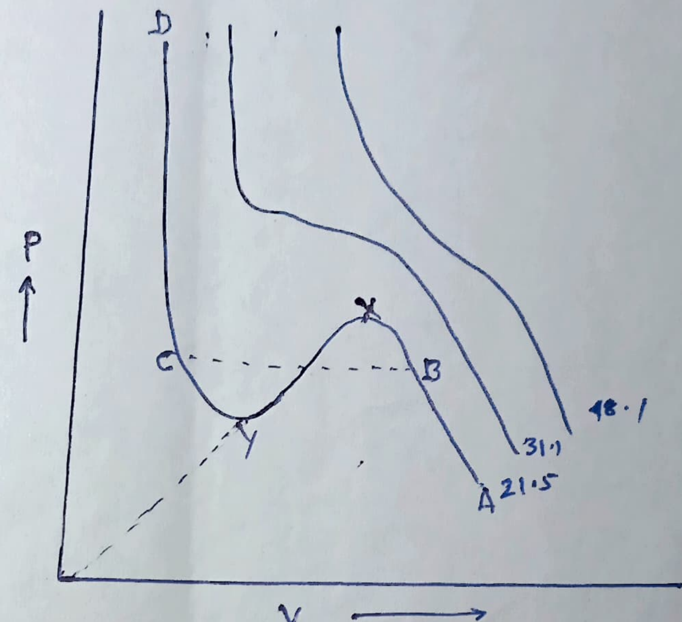
Critical Constants and its relation with Vander Waal's Constant

Application of Vander Waal's equation to critical phenomenon.

Critical Constants :- A gaseous state is defined by P, V and T. Generally one of them, particularly the temperature T is maintained constant. The curve showing the variation of volume (V) at constant temperature (T) with pressure P are called Isotherms.

Andrews plotted the isotherms for CO_2 at various temperatures are shown in fig. given below.



A certain temperature called Critical Temp T_c above which it can not be liquified no matter how great the pressure may be. The T_c value for CO_2 is 30°C and therefore above 30°C liquid CO_2 does not at all exist. The pressure and volume at this temp. is called Critical Pressure P_c and Critical Volume V_c. i.e Every gas when it is above a critical temp. can not be liquified.

Critical temp. of Oxygen is −18°C.

The Vander Waal's equation for real gas is given as

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

or, $$PV-bP+\frac{a}{V}-\frac{ab}{V^2}=RT$$

Multiplying throughout by $\frac{V^2}{P}$ we get

$$V^3-V^2b+\frac{aV}{P}-\frac{ab}{P}-\frac{RTV^2}{P}=0$$

or, $$V^3-\left(b+\frac{RT}{P}\right)V^2+\frac{aV}{P}-\frac{ab}{P}=0$$

When $T = T_c$ and $P = P_c$, then

$$V^3 - \left(\frac{b + RT_c}{P_c}\right)V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \qquad \text{--- (1)}$$

At Critical Points, $V = V_c$ or, $V - V_c = 0$

$$(V - V_c)^3 = 0$$

or, $$V^3 - 3V^2V_c + 3V_c^2V - V_c^3 = 0 \qquad \text{--- (2)}$$

On equating the powers of V in eqn (1) and (2) we get

$$3V_c = \frac{RT_c}{P_c} + b \qquad \text{--- (3)}$$

$$3V_c^2 = \frac{a}{P_c} \qquad \text{--- (4)}$$

or, $$a = 3P_cV_c^2 \qquad \text{--- (5)}$$

$$V_c^3 = \frac{ab}{P_c} \qquad \text{--- (6)}$$

Dividing eqn (6) by eqn (4)

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

or $$V_c = 3b \qquad \text{--- (7)}$$

Putting this value in eqn (4), we have.

$$3 \times (3b)^2 = \frac{a}{P_c}$$

$$P_c = \frac{a}{27b^2} \qquad \text{--- (8)}$$

or $$a = 27b^2 P_c \qquad \text{--- (9)}$$

Putting the value of V_c and P_c in equation (3) we get

$$3 \times 3b = \frac{RT_c}{a/27b^2} + b$$

$$= \frac{R \times 27b^2 T_c}{a} + b$$

or $$9 = \frac{R \times 27 \cdot b \cdot T_c}{a} + 1$$

$$8 = \frac{27RbT_c}{a} \quad \text{or} \quad T_c = \frac{8a}{27Rb} \qquad \text{--- (10)}$$

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

$$b = \frac{8 \times 27 b^2 P_c}{27 R \cdot T_c}$$

$$1 = \frac{8 b P_c}{R T_c}$$

$$\text{or } b = \frac{R T_c}{8 P_c} \qquad \text{——— (11)}$$

Hence we can Calculate the Values of Vanderwaal's Constant 'a' and 'b' if Critical Pressure, Critical Volume and Critical Temperature i.e P_c, V_c and T_c are known.

Similarly P_c, V_c and T_c Can be Calculated if Vanderwaal's Constant 'a', and 'b' are known.