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(I) Critical Phenomenon and

(II) Determination of Critical constants from Vanderwaals equation.

(III) Principle of corresponding state/equation for reduced state

(I) A gas can be liquified by lowering the temperature and increasing the pressure. At the lower temperature, the gas molecules lose their kinetic Energy and they are converted into liquid.

Andrew established that for every gas there is a temperature below which a gas can be liquified and this temperature is called critical temperature (T_c) of the gas.

Critical Pressure (P_c) is the minimum pressure required to liquify the gas at critical tempr. (T_c) Likewise the critical volume (V_c) is the volume occupied by a mole of a gas at critical temperature.

It is clear that all real gases have critical constants. At critical tempr. and critical pressure the gas becomes identical with its liquid and is said to be in critical state.

(II) Relation between critical constants and Vanderwaals constants:—

According to Vanderwaal's equation for one mole of a gas

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

Where p = pressure of the gas

V = volume of the gas

a = coefficient of attractive forces between gas molecules

and b = four times the actual volume of the gas

The above equation can be written as

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiply this equation by $\frac{V^2}{P}$, we get

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

$$V^3 - V^2\left(b + \frac{RT}{P}\right) + \frac{a}{P} V - \frac{ab}{P} = 0 \quad \cdots \text{(ii)}$$

At critical Point, the roots of Vander waal's equation are real and identical. This value of 'V' is called critical volume and is denoted by V_c ie $V = V_c$

or $\quad V - V_c = 0$

on cubing both sides

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

or, $$V^3 - 3V^2 V_c + 3V \cdot V_c^2 - V_c^3 = 0 \quad \cdots \text{(iii)}$$

Let P_c and T_c be the critical Pressure and critical temperature respectively, then from equation (ii)

$$V^3 - V^2\left(b + \frac{RT_c}{P_c}\right) + \frac{a}{P_c} V - \frac{ab}{P_c} = 0 \quad \cdots \text{(iv)}$$

Equating the power of 'V' in equation (iii) and (iv)

$$\cancel{3V_c = b +}$$

$$3V_c = b + \frac{RT_c}{P_c} \quad \cdots \text{(V)}$$

$$3V_c^2 = \frac{a}{P_c} \quad \cdots \text{(vi)}$$

(III) Principle of corresponding states
or
Derivation of law of corresponding states / equ^n for reduced state

If P, V and T be the pressure, volume and temperature of a gas respectively and P_c, V_c and T_c their respective critical values, then the ratio of P to P_c, V to V_c and T to T_c are called reduced pressure, reduced volume and reduced temperature respectively.

Let $\frac{P}{P_c} = \pi$ (Reduced pressure)

$\frac{V}{V_c} = \phi$ (Reduced volume)

and $\frac{T}{T_c} = \theta$ (Reduced temperature)

Thus, the Vander Waal's equation $\left(P+\frac{a}{V^2}\right)(V-b) = RT$ may be written as

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R.\theta T_c$$

Put the value of P_c, V_c and T_c in terms of 'a' and 'b'

$$\left(\pi . \frac{a}{27b^2} + \frac{a}{9\phi^2 b^2}\right)(3\phi b - b) = R\theta \frac{8a}{27Rb}$$

or, $$\frac{ab}{27b^2}\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \frac{a}{27b}$$

or, $$\frac{a}{27b}\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \frac{a}{27b}$$

or $$\boxed{\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta}$$

This equation is called reduced equation of state.

This equation is free from a, b, P_c, V_c, T_c, and R and hence is applicable to all substances in the gaseous and liquid states.

This equation shows that "When two substances have the same reduced temperature and pressure, they must have the same reduced volume i.e. they are in corresponding states."

The boiling points of liquids are approximately $\frac{2}{3}$rd of their critical temperature. Therefore, almost all liquids are in corresponding states at their boiling points.

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$$V_c^3 = \frac{ab}{P_c} \quad \cdots\cdots \quad (vii)$$

divide equation (vii) by equation (vi)

$$\frac{V_c^3}{3V_c^2} = \frac{ab}{P_c} \div \frac{a}{P_c}$$

$$= \frac{ab}{P_c} \times \frac{P_c}{a}$$

or $\boxed{V_c = 3b}$

Put the value of V_c in equation (vi)

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

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

Now put the value of P_c and V_c in equation (V)

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

or $$9b = b + \frac{RT_c}{a/27b^2}$$

or $$8b \times \frac{a}{27b^2} = RT_c$$

$$\boxed{T_c = \frac{8a}{27Rb}}$$

Thus $$R\frac{T_c}{P_c V_c} = R \cdot \frac{8a}{27Rb} \times \frac{27b^2}{a} \times \frac{1}{3b}$$

$$= \frac{8}{3}$$

or, $\boxed{\frac{P_c V_c}{T_c} = \frac{3}{8} R}$

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