Law of Corresponding States

If the values of P, V and T be expressed as fraction of Corresponding Critical values, we get.

$$P/P_c = P_r, \quad \frac{V}{V_c} = V_r \quad \text{and} \quad \frac{T}{T_c} = T_r$$

Where P_r, V_r and T_r are called reduced Pressure, Volume and Temperature respectively,

therefore, $P = P_r \cdot P_c$, $V = V_r \cdot V_c$ and $T = T_r \cdot T_c$

Replacing P, V and T in Vander Waal's equation for real gases

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

$$\left\{P_r P_c + \frac{a}{V_r^2 V_c^2}\right\}(V_r V_c - b) = R\,T_r T_c$$

On Putting the value of Critical Constants, we have

$$\left\{P_r \cdot \frac{a}{27b^2} + \frac{a}{V_r^2 9b^2}\right\}(V_r 3b - b) = \cancel{R} T_r \cdot \frac{8a}{27\cancel{R}b}$$

$$\left\{P_r \cdot \frac{a}{27b^2} + \frac{a}{9b^2 V_r^2}\right\} b(3V_r - 1) = T_r \cdot \frac{8a}{27b}$$

$$\text{or,} \quad \left\{\frac{P_r \cdot a}{27b} + \frac{a}{9bV_r^2}\right\}\{3V_r - 1\} = T_r \cdot \frac{8a}{27b}$$

Multiplying throughout by $27b/a$ we have

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \qquad \text{——— (1)}$$

The above eqn (1) is completely free from Constants such as R, a and b, hence this is applicable to all substances in fluid state. Two or more substances having identical P_r, V_r and T_r are said to be Corresponding state. This is also called Law of Corresponding states

As b.Ps of liquids are approximately $\frac{2}{3}$rd of their T_c's. It means that liquids at their b Ps are approximately in their Corresponding states.