

Law of Corresponding States:

Reduced equation of state & law of Corresponding state: $\rightarrow$

Reduced equation state:

There are two constants in Vanderwaal equation i.e. 'a' & 'b', the value of these constants changes with change in gas. or we can say as gas changes the value of Vanderwaal constant 'a' & 'b' also changes. In this condition we should have different equations for different gases. If we write the relative values in terms of Critical Constants (P_c , V_c & T_c) respectively for actual pressure, volume, & temperature then we have an equation free from any such constants and so it can be applied for all the gases.

$$\text{Let. } \frac{P}{P_c} = P_r, \frac{V}{V_c} = V_r \text{ \& } \frac{T}{T_c} = T_r.$$

Where P_r , V_r & T_r are also called reduced values of pressure, volume & temperature respectively which are pure numbers & dimensionless also.

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

When we use critical constant in the vanderwaal equation for 1 mol of gas

$$\left(P + \frac{3P_c \times V_c^2}{V^2}\right)\left(V - \frac{V_c}{3}\right) = \frac{8}{3} \cdot \frac{P_c V_c}{T_c} \cdot T \quad \text{--- I}$$

Divide both side by $P_c V_c$ we have

$$\Rightarrow \left[\frac{P + \frac{3P_c V_c^2}{V^2}}{P_c} \right] \left[\frac{V - \frac{V_c}{3}}{V_c} \right] = \frac{\frac{8}{3} \frac{P_c V_c T}{T_c}}{P_c \times V_c}$$

$$\Rightarrow \left[\frac{P}{P_c} + 3\left(\frac{V_c}{V}\right)^2 \right] \left[\frac{V}{V_c} - \frac{1}{3} \right] = \frac{8}{3} \frac{T}{T_c}$$

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

$$\text{or } \left[\left(P_r + \frac{3}{V_r^2}\right)(V_r - 1) = 8 T_r \right] \quad \text{--- II}$$

The above equation II is called reduced equation of state or reduced vanderwaal equation of state. If the value of P_r , V_r & T_r are appropriate then it hold good for all gases without any constant values.

Teacher's Signature: _____

If the two or more than two gases reduced pressure & reduced temperature values are same then they should have same reduced volume also. This statement is also called Law of Corresponding State.

By plotting Compressibility factor $Z = \left(\frac{PV}{RT} \right)$ against reduced pressure (P_r) the law of Corresponding State can be checked experimentally for different gases at same reduced temperature (T_r). The value of Z for different gases seems to be same curve, this proves all gases in Corresponding State deviate almost same from ideal behaviour.

Boiling point of all liquids are approximately two third of their ~~critical~~ critical temperature. It proves the liquid at their boiling point are in Corresponding State. Hence we can say when we study the physical properties of liquids and their chemical constitution then their properties are determined at their boiling point.