*. Molecular Viscosity & RHEOCHOR :-

Dunstan discovered an interesting relationship between viscosity and molar volume of non-associated liquids as:

$$\frac{d}{M} \times \eta \times 10^6 = 40 \text{ to } 70 \qquad \text{—— (1)}$$

Where, d = density
M = molecular weight
η = coefficient of viscosity of liquid.

The above relationship has been employed to know whether a liquid is associated or not. If the value exceeds 70, the liquid exists as associated molecules.

since, $\frac{M}{\rho} = V_m$ (molecular volume)

The surface area of one mole of liquid or molar surface is $\left(\frac{M}{\rho}\right)^{2/3}$

$\therefore$ Molecular viscosity = Molar surface × viscosity

$$= \left(\frac{M}{\rho}\right)^{2/3} \times \eta$$

The molecular viscosity is an additive and constitutive property at the boiling point of liquid.

RHEOCHOR :-

Newton friend suggested another constant Rheochor (γ) which is both additive and constitutive. It is obtained by multiplying the molecular volume of the liquid by eight root of its viscosity at the same temperature.

Mathematically,

$$\gamma = \frac{M}{\rho} \times \eta^{1/8}$$

The Rheochor may be regarded as molecular volume of a liquid at temperature at which the viscosity is equal to unity.

$$\gamma = \frac{M}{\rho} = V_m$$ (when η = unity)

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* Internal Pressure :-

In a liquid, the molecules are separated from each other by a distance of the order of molecular magnitude. So, that the force of attraction must be considered. At very closer distance, when the molecules touch, their will be very high repulsion. The factors responsible for this are their finite size and repulsion between the positive nucleus and negative electron clouds of the molecules. Thus, there is a balance between the attractive and repulsive force in the interior of a liquid. This is called the <u>internal pressure</u>.

The repulsive force try to increase the volume. Let 'U' is the internal energy then, $\left(\frac{dU}{dV}\right)_T dV$ is the change in energy resulting from an increase in volume.

Thus, Internal pressure

$$P_i = \left(\frac{dU}{dV}\right)_T \qquad \text{——— (1)}$$

It is shown in thermodynamics that —

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{dP}{dT}\right)_V - P \qquad \text{——— (2)}$$

The external pressure $(P) << P_i$

$$\therefore \quad P_i = \left(\frac{dU}{dV}\right)_T = T\left(\frac{dP}{dT}\right)_V \qquad \text{——— (3)}$$

P_i is the resultant of attractive and repulsive force, it depends markedly on volume i.e. external pressure.