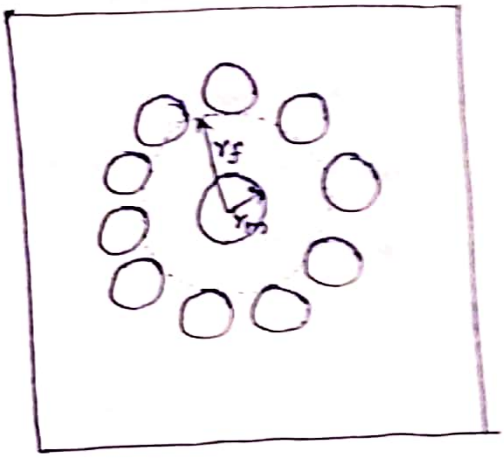
* Free Volume in liquid :-

In a liquid the molecules move over an infinitesimally small distance before colliding with one another. This is due to the fact that each molecule in a liquid is tightly surrounded by almost 10 to 12 neighbours forming a sort of spherical cage which can be approximated to a spherical box of radius r_f which is only slightly bigger than the enclosed molecule of radius r_m. It is evident that the centre of the caged molecule can move about in a very small volume. This volume of a mole of molecule is known as free volume.



Thermodynamically it can be shown that the magnitude of the free volume is approximately 0.37 cm^3. The free volume per molecule is thus equal to 0.61 Å. Thus we have—

$$(4/3)\pi r_f^3 = 0.61\,Å$$

Where r_f = 0.54Å.

* Vapour Pressure :-

The vapour pressure of a liquid at a given temperature is defined as the pressure of the vapour in equilibrium with the liquid at that temperature.

The vapour pressure measures the ease with which a liquid can be converted into vapour. i.e. it is a measure of the volatility of the liquid. It is a measure of the escaping tendency of a molecules from the surface of the liquid.

As the temperature rises, the number of molecules escaping from the liquid surface increases and there is increase in the no. of vapour molecules in the space above the liquid when phase equilibrium is attained. Hence, vapour pressure of a liquid increases with rise in temperature.

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* Heat of Vaporisation :-

When a liquid changes in to vapour state, the intermolecular forces have to be come. Hence, a certain amount of energy has to be supplied to the liquid in the form of heat. The quantity of heat which has to be supplied to one mole of liquid at its boiling point so as to change it into vapour state at the same temperature, is known as the molar heat of vaporisation. (ΔH_{vap}).

The molar heat of vaporisation of a liquid expressed in Joules divided by the normal boiling point of the liquid on the absolute scale is approximately equal to 88. This is known as Trouton's Rule.

This may be expressed as:

$$\frac{\Delta H_{vap}}{T_b} \simeq 88 \ J \ K^{-1} \ mol^{-1}.$$

This equation is only approximate as the values of $\Delta H_{vap}/T_b$ are seen to vary over a wide range viz. from about 60 to 110 $J \ K^{-1} \ mol^{-1}$.

The quantity $\Delta H_{vap}/T_b$ is also called entropy of vaporisation ΔS_{vap}.

Trouton's Rule is useful for estimating the heat of vaporisation of a liquid if its boiling point is known.