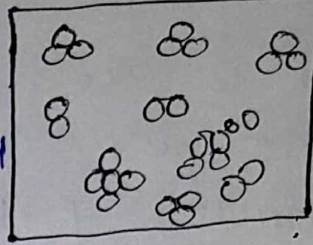
Vacancy theory of Liquids :-

A liquid is generally less dense than the solid.



⇒ The intermolecular space in a liquid is more than that of solid.

- Eyring and Ree proposed a simple theory that the internuclear space in liquid is not ran-
domly distributed but contains molecular
sizes holes or vacancies. The liquid is consi-
dered as a random congregation of molecules
and these holes.

It is assumed that the molecules surrounding a
given hole can easily jump into it and are
thus gas like where as those in immediate
contact with the hole are solid-like.

If V_l and V_s are the respective molar volume
of the liquid and the solid then

$$\frac{\text{No. of holes}}{\text{No. of molecules}} = \frac{V_l - V_s}{V_s}$$

The probability that a hole confers gas-like
properties on it's neighbouring molecule is
proportional to the fraction of neighbouring

Positions accupied by the molecules.
for random-distribution of holes, the ratio is given by V_s/V_l.

Hence $$x_g = \left(\frac{V_l - V_s}{V_s}\right)\left(\frac{V_s}{V_l}\right)$$

=) $$x_g = \frac{V_l - V_s}{V_l}$$

and

$$x_s = \frac{V_s}{V_l} \quad [\because 1 - x_g = x_s]$$

where x_g and x_s are the mole fraction of the gas-like and solid like molecules, respectively.
Based on these ideas, Eyring and Ree Calculated the melting point, b.p and critical constants and some thermodynamic properties of Argon. The agreement of theory with experiments was found to be quite satisfactory.

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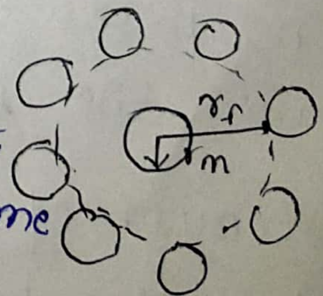
free volume in a liquid :-

In a liquid the molecules move over an infinite-simly 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 approximated to a spherical box of radius r_f which is only slightly bigger than 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 for a mole of molecules is known as 'free volume.'



Thermodynamically, the magnitude of free volume is approximately 0.37 cm3

The free volume per molecule is thus equal to $0.61\ \text{Å}^3$

$\Rightarrow \frac{4}{3}\pi r_f^3 = 0.61\ \text{Å}^3 \Rightarrow r_f = 0.54\ \text{Å}$

The radius r_f represents the average distance travelled by a molecule b/w collisions with the walls of the spherical cage.

Average speed $\approx 3 \times 10^4\ cm\ s^{-1}$ $\Rightarrow$ collision per second = 5.6×10^{12} with the spherical cage