* 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 internal pressure.

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

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

It is shown in thermodynamics that —

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

The external pressure $(P) << P_i$

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

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

* Solubility Parameters :-

The solubility parameter is a numerical value that indicates the relative solvency behaviour of a specific solvent. It is derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporization.

J.H. Hildebrand proposed the square root of the cohesive energy density as a numerical value indicating the solvency behaviour of a specific solvent.

Thus

Solubility parametre -

$$\delta = \left[\frac{\Delta H - RT}{V_m}\right]^{1/2}$$

Where, ΔH = Heat of vaporisation

R = Gas constant

T = Temperature

V_m = molar volume.

The cohesive energy density of a liquid is a numerical value that indicating the energy of vaporisation in calories per cubic centimeter and is a direct reflection of the degree of Vanderwaals forces holding the molecules of the liquid together.

The cohesive energy density is given by -

$$C = \frac{\Delta H - RT}{V_m}.$$

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