

* Conditions for validity of distribution law:-

The distribution law is valid only if the following conditions are satisfied -

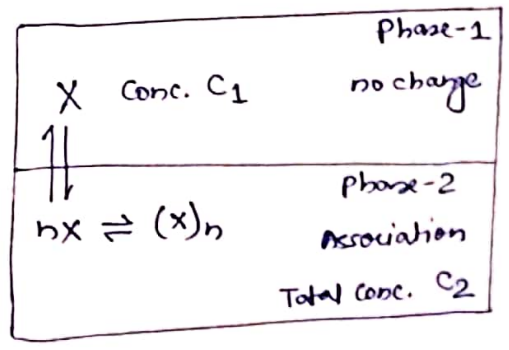
- (i) The temperature should remain constant throughout the measurement.
- (ii) The two solvents should be mutually immiscible or very sparingly soluble with each other.
- (iii) The solute should not change the solubility of two liquids in each other.
- (iv) Solute doesn't react with the solvents.
- (v) The solute remains in the same molecular state i.e. solutes should not either associate or dissociate in a given solvent.

* Modification of distribution law for association:-

When the solute associates in one of the phase (solvent)

Let us suppose that a solute has its molecular formula 'X' in phase-1 & exists as both X & X_n (Associated form of X) in phase-2.

The concentration of X in phase-1 is C₁ mol/L and the total concⁿ acts in phase-2 is C₂ mol/L.



On applying the law of mass action -



$$K = \frac{[X_n]}{[X]^n}$$

$$\text{or } [X]^n = \frac{1}{K} [X_n]$$

$$\text{or } [X] = \text{Const.} \cdot \sqrt[n]{X_n}$$

If most of the solute remains in the associated form as X_n in phase-2. Then,

$$[X_n] = C_2$$

From distribution law -

$$K = \frac{\text{Conc}^n \text{ of } X \text{ in phase-1}}{\text{Conc}^n \text{ of } X \text{ in phase-2 which remains as } X_n}$$

$$K = \frac{C_1}{\sqrt[n]{C_2}}$$

The value of 'n' i.e. the degree of association or extent of complexity of solute molecules in one of the phases can be calculated by any one of the following methods -

(i) Hit & Trial method :-

The value of C_1 & C_2 obtained experimentally are substituted in the equation -

$$K = \frac{C_1}{\sqrt[n]{C_2}}$$

now, putting $n = 2, 3, 4, 5, \dots$ etc. one by one.

The values of k can be calculated. The value for which a nearly constant value of k is obtained is equal to n .

(ii) Graphical methods —

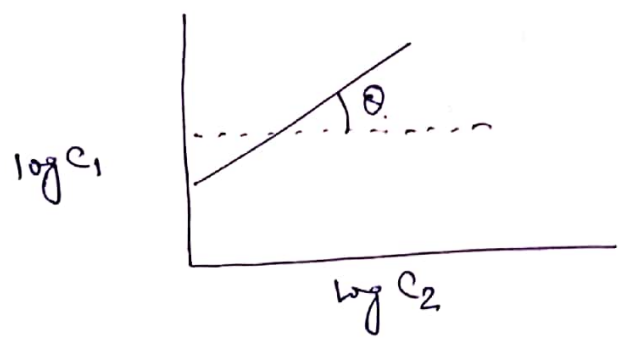
Since, $k = \frac{C_1}{n\sqrt{C_2}}$

taking log on both sides —

$$\log k = \log C_1 - \log (C_2)^{1/n}$$

$$\log k = \log C_1 - \frac{1}{n} \log C_2$$

$$\log C_1 = \frac{1}{n} \log C_2 + \log k$$



$n = \text{slope}$
 $\tan \theta = \frac{1}{n}$

From,
Ajay Kumar Gupta.
L.S. College (chemistry)