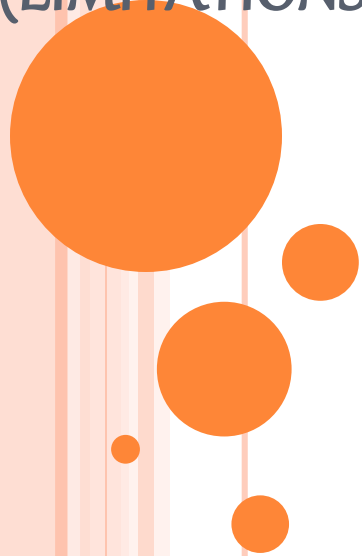


DISTRIBUTION LAW  
(LIMITATIONS AND APPLICATIONS)

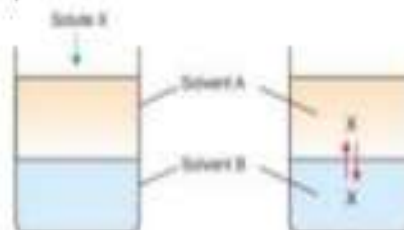


# Nernst's Distribution Law

Nernst gave a generalization governing the distribution of a solute between **two non-miscible solvents**. This is called **Nernst's Distribution law** or **Nernst's Partition law** or simply **Distribution law** or **Partition law**.

**Statement of Nernst's distribution law:** If a solute **X** distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,

Then 
$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = K_D$$



If  $C_1$  denotes the concentration of the solute (**X**) in solvent, A and  $C_2$  the concentration in solvent B, then Nernst's Distribution law can be expressed

as 
$$\frac{C_1}{C_2} = K_D$$

The constant  $K_D$  (or simply  $K$ ) is called the **Distribution coefficient** or **Partition coefficient** or **Distribution ratio**.

## **PROBLEM 1.**

*A solid X is added to a mixture of benzene and water. After shaking well and allowing to stand, 10 ml of the benzene layer was found to contain 0.13 g of X and 100 ml of water layer contained 0.22 g of X. Calculate the value of distribution coefficient.*



## SOLUTION 1 -

*Concentration of X in benzene ( $C_b$ ) =  $0.13 / 10 = 0.013 \text{ g ml}^{-1}$*

*Concentration of X in water ( $C_w$ ) =  $0.22 / 100 = 0.0022 \text{ g ml}^{-1}$*

*According to Distribution law :*

$$C_b / C_w = 0.013 / 0.0022 = 5.9$$



# SOLUBILITIES AND DISTRIBUTION LAW

When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, we can write the distribution law as

$$C_1/C_2 = S_1/S_2 = K_D$$

where  $S_1$  and  $S_2$  are the solubilities of the solute in the two solvents.

Hence knowing the value of the Distribution coefficient ( $K_D$ ) and the solubility of solute in one of the solvents, the solubility of solute in the second solvent can be calculated.



## **Effect of Ionic Dissociation and Molecular Association on Partition:**

- During distribution, the solute may get associated into molecules in one liquid phase or may get dissociated into ions in either of the liquid phase.
- The distribution law states that: ‘the ratio of undissociated or unionised solute which is distributed between the two immiscible phases is at equilibrium’. This is known as partition coefficient (K).
- The distribution law applies only to the concentration of the species common to both phases, namely, the *monomer* or simple molecules of the solute.

# Limitations <sup>4</sup>

- **Dilute solutions:** The conc. of solute must be low in two solvents. This law does not hold good when the concentrations are high.
- **Constant temperature:** Temperature should be kept constant throughout the experiment, since solubility is dependent on temperature.
- **Same molecular state:** Solute must be in the same molecular state in both the solvent.
- **Equilibrium concentration:** This is achieved by shaking the mixture for longer time.
- **Non-miscibility of solvents:** So, the solvents are to be allowed for separation for a sufficient time.

## APPLICATION OF DISTRIBUTION LAW

- There are numerous applications of distribution law in the laboratory as well as in industry

### (1) Solvent Extraction-

This is the process used for the separation of organic substances from aqueous solutions. The aqueous solution is shaken with an immiscible organic solvent such as ether (or benzene) in a separatory funnel. The distribution ratio being in favour of ether, most of the organic substance passes into the ethereal layer. The ethereal layer is separated and ether distilled off. Organic substance is left behind.





## **2) Partition Chromatography**

A paste of the mixture is applied at the top of a column of silica soaked in water. Another immiscible solvent ( hexane) is allowed to flow down the column. Each component of the mixture is partitioned between the stationary liquid phase (water) and the mobile liquid phase (hexane). The various components of the mixture are extracted by hexane in order of their distribution coefficients.



### **(3) Desilverization of Lead (*Parke's Process*)**

When molten zinc is added to molten lead containing silver (*argentiferous lead*), zinc and lead form immiscible layers and silver is distributed between them. Since the distribution ratio is about 300 in favour of zinc at 800° C, most of silver passes into the zinc layer. On cooling the zinc layer, an alloy of silver and zinc separates. The Ag-Zn alloy is distilled in a retort when zinc passes over leaving silver behind. The lead layer still contains unextracted silver. This is treated with fresh quantities of molten zinc to recover most of the silver



## **(4) Confirmatory Test for Bromide and Iodide**

The salt solution is treated with chlorine water. Small quantity of bromine or iodine is thus liberated. The solution is then shaken with chloroform. On standing chloroform forms the lower layer. The free bromine or iodine being more soluble in chloroform concentrates into the lower layer, making it red for bromine and violet for iodine.



## 5) Determination of Association

When a substance is associated (or polymerized) in solvent A and exists as simple molecules in solvent B, the Distribution law is modified as

$$n\sqrt[n]{C_a/C_b} = k$$

when  $n$  is the number of molecules which combine to form an associated molecule.



## (6) Determination of Dissociation

Suppose a substance X is dissociated in aqueous layer and exists as single molecules in ether.

If x is the degree of dissociation (or ionisation), the distribution law is modified as

$$C_1 / C_2 (1-x) = K$$

where  $C_1$  = concentration of X in benzene

$C_2$  = concentration of X in aqueous layer

The value of x can be determined from conductivity measurements, while  $C_1$  and  $C_2$  are found experimentally. Thus the value of K can be calculated. Using this value of K, the value of x for any other concentrations of X can be determined.



## (7) Determination of Solubility

Suppose the solubility of iodine in benzene is to be determined. Iodine is shaken with water and benzene. At equilibrium concentrations of iodine in benzene ( $C_b$ ) and water ( $C_w$ ) are found experimentally and the value of distribution coefficient calculated.

$$C_b / C_w = K_d$$

$$S_b / S_w = K_d$$

where  $S_b$  = solubility in benzene; and  $S_w$  = solubility in water.



THANK YOU

