THE DISTRIBUTION OR PARTITION LAW

If to a system of 2 phases made up of 2 immiscible, or only slightly miscible, components existing as 2 distinct liquid layers, there is added a third substance soluble in both layers, then the added substance will distribute itself between the 2 phases in such a way that the ratio of its concentrations in each phase is constant and independent of the amount of added substance provided that this substance exists in the same type of molecular species in each phase.

Thus:

$$\frac{\text{Concentration of solute X in solvent A}}{\text{Concentration of solute X in solvent B}} = K \tag{1}$$

Where K = Distribution or Partition Coefficient.

e.g. Distribution Coefficients. Concentrations in moles/litre.

Iodine between $C\,Cl_4$ (i) and H_2O (ii)

C_i	C_{ii}
0.08	86.0

The Distribution Coefficient is only constant when the solute exists in the same type of molecular species in both solvents. If this is not the case then the numerical value of the distribution coefficient will vary with any variation in the solution concentration, e.g. distribution of acetic acid between $C\,Cl_4$ and H_2O.

Concentration in $C\,Cl_4$	Concentration in H_2O	Distribution Coefficient	
C_i	C_{ii}	C_i/C_{ii}	$\sqrt{C_i/C_{ii}}$
0.0096	0.684	0.0140	0.143
0.0187	1.021	0.0183	0.132
0.0460	1.691	0.0266	0.127

Thus the ratio of C_i/C_{ii} is not constant, but increases as the concentration rises. It will be recalled that acetic acid exhibits association in certain solvents. Thus, it has a normal MW in aqueous solution but twice the normal MW in carbon tetrachloride. In this latter solvent the following equilibrium will exist:

$$\underset{(1-\alpha)c}{(CH_3COOH)_2} \rightleftharpoons \underset{2\alpha c}{2\ CH_3COOH}$$

If the initial concentration of double molecules is c, and if a fraction α is dissociated into single molecules, then on application of the Law of Mass Action:

$$K = \frac{(2\alpha c)^2}{(1-\alpha)c}$$

$$= \frac{4\alpha^2c^2}{(1-\alpha)c}$$

$$= \frac{4\alpha^2c}{(1-\alpha)}$$

Therefore: $$\alpha^2 = \frac{K(1-\alpha)}{4c} \tag{2}$$

If the numerical value of α is small, then $(1-\alpha)$ may be taken as unity. Thus equation (2) is capable of simplification:

$$\alpha^2 = \frac{K}{4c} \qquad (3)$$

so that α varies as $\frac{1}{\sqrt{c}}$ and in the specific case of acetic acid distributed between carbon tetrachloride and water

$$\alpha c = \text{Constant} \times c \times \frac{1}{\sqrt{c}}$$

$$= \text{Constant} \times \sqrt{c} \qquad (4)$$

If the concentration in $C\,Cl_4$ is denoted by C_i and the concentration in water by C_{ii}, then the distribution coefficient

$$\sqrt{C_i/C_{ii}}$$

should be constant.

Extraction of a Solute with a Second Solvent

This is dependent upon the distribution of a solute between 2 partially miscible or immiscible liquids. In this process a solution of the solute in question is shaken up with a second solvent in which the solute is more soluble. The solute then distributes itself between the 2 solvents, forming solutions which are capable of ready separation. Since the solubility of such substances is usually greater in organic solvents than in water, it is common practice to employ organic solvents for the second solvent. Also, since the solubility of organic compounds is lower in aqueous solutions of electrolytes than pure water, electrolytes are commonly added to facilitate still further the extraction process. In other words, the organic solute tends to be 'salted out' from its aqueous solution.

The efficiency of extraction under given conditions may be calculated:

Let a ml of a solution (Phase I) containing c gm of a dissolved solute be extracted repeatedly with b ml of a second solvent (Phase II).

If after the first extraction the weight of solute remaining in Phase I is c_i gm, then the concentration per ml in Phase I will be c_i/a, whilst that in Phase II is $(c-c_i)/b$. Thus be application of the Distribution law:

$$\frac{c_i/a}{(c-c_i)/b} = K \qquad (5)$$

Thus:

$$c_i = c\,\frac{Ka}{Ka + b} \qquad (6)$$

If after a second extraction, c_2 gm of the solute remain dissolved in Phase I, then:

$$c_2 = c_i\,\frac{Ka}{Ka + b} \qquad (7)$$

$$= c\left(\frac{Ka}{Ka + b}\right)^2 \qquad (8)$$

Equation (8) is capable of generalization, so that after the nth extraction, the weight, c_n gm of solute remaining in Phase I is:

$$c_n = c\left(\frac{Ka}{Ka + b}\right)^n \qquad (9)$$

In practice it is more efficient to use a number of small portions of the extracting solvent in a number of individual extractions, rather than use the whole of this solvent in a single extraction.

Complete extraction is impossible since although the quantity

$$\left(\frac{Ka}{Ka + b}\right)^n$$

in equation (9) becomes progressively smaller as the number of extractions increase, it never actually becomes zero.