The Theory of Ion-Distribution Coefficients, Their Determination and Use

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One of the subjects which have always commanded the interest of chemists is the question of the *solubility* of the substances. What forces are here at work, and how may solubility be computed quantitatively?

In the 19th century, *thermodynamics* led us many paces forward along the way, but did not lead us to the core of the problem. The true understanding of the problems of solubility will not be gained from thermodynamics, but only from the more comprehensive atomistics, of which thermodynamics, in spite of its own great importance, is but a single side issue.

The problem of the solubility of a solid substance in a liquid divides naturally into two parts. The first deals with the *structure of the solid substance*, the second with the *properties of the solution*. This becomes apparent when the solution process takes place through evaporation. To compute the vapour pressure of the solid substance, it is necessary to know the work required to transform one molecule of the solid substance into the vapour state. This work depends on the crystalline structure of the substance. Going further, to determine the solubility from the vapour pressure, it is necessary to know the work required to transfer one molecule from the solution to the vapour state. This work depends on the properties of the solution.

Limiting our considerations to the strong electrolytes built up from stable ions, we find in the modern ion-lattice theory, especially developed by Born, an approximate theory for the work done when ions are transferred from the solid crystal into the vapour state. When, in what follows, we study the distribution of ions between two liquids, we are in reality studying the last mentioned work. The distribution between a liquid and its vapour may be considered a simple example of distribution between two liquids.

I

Let us first look more closely at the *definition and determination of the distribution coefficients.*

The definition of a distribution coefficient is simple enough in the case of two immiscible media. However, if the two media are miscible, as for instance, water and alcohol, the definition is slightly more difficult. We may define thus: *The distribution coefficient is the ratio between the concentrations of the soluble substance in solutions in which the dissolved substance has the same activity.* Solutions, in which the dissolved substance has the same activity, are, for instance, solutions saturated with the same solid substance, or in which the dissolved substance has the same vapour tension.

Each of the ions in an electrolyte has its own special distribution coefficient. The distribution coefficient of an electrolyte, which can be computed from its solubility in two media, lies between those of the two ions, and in the case of binary electrolytes, it equals the square root of the product of the individual distribution coefficients.

Table 1. The sum of the ion-distribution exponents between water and alcohol for different salts, computed from the solubilities of the salts in water and alcohol

	Li	Na	K	Rb	Cs	NH$_4$	N(CH$_3$)$_4$	N(C$_2$H$_5$)$_4$	Ag
Cl		6.0	6.6	6.4		5.2			
Br		5.8				(5.1)			
J		5.5				(5.9)	4.4	4.1	
ClO$_4$	(5.1)	4.6	4.6	4.6	4.7	4.1			
Benzoate	4.1	4.8				3.6			2.3
Salicylate		4.9				(5.2)			
Laurate	0.4								
Myristate	—0.7								0.1
Palmitate	—0.9								—0.2
Stearate	—1.2								—0.2

In table 1, Dr. Larsson and I have compiled a number of results about the ion-distribution coefficients between water and alcohol. The figures are computed from the results of *solubility experiments* (concentration in water in the numerator). Instead of the actual distribution coefficient V, its logarithm is given in the table; this is designated P and named the distribution exponent:

$$P = \log V$$

From solubility determinations it is impossible to calculate the distribution exponents of the individual ions, but the *sum of the distribution exponents of the ions* may be calculated; it is this sum which is given in the table.

The figures make no great claim to exactitude. In the first place many of the solubility determinations are uncertain. Often the alcohol used contained water; neither is it absolutely certain in all cases that the solid form, whose solubility was determined, was the anhydrous unsolvated salt which is a presupposition for the exactness of the calculations. However our attention has been drawn to this point (moreover, through determinations of the vapour pressure of the solvates, it is possible to utilize also solubility determinations of solid hydrated salts in determining distribution coefficients).

The greatest inexactitude of the computations is due to a special characteristic of the distribution coefficients of the electrolytes. On account of inter-ionic forces, and in contrast to the case of non-electrolytes, the distribution coefficient of the electrolytes *depends greatly upon concentration.*

The value listed in the table, is when possible that limiting value which the distribution exponent approaches under increasing dilution.

If the distribution coefficient between water and alcohol, calculated directly from the solubilities, is called V, it is possible to compute the limiting value for infinitely dilute solutions (V_0) according to the following equation:

$$V_0 = V \frac{F_{H_2O}}{F_A}$$

in which F_{H_2O} and F_A are the activity coefficients in the saturated aqueous and saturated alcoholic solutions, respectively.

Potassium chloride is that salt for which the sum of the ion-distribution exponents has the highest value (6.6). An aqueous solution of this salt must be

$$10^{\frac{6.6}{2}} = 2000$$

times more concentrated than an alcoholic solution, before distribution equilibrium (the same activity of the salt in the two solutions) is attained.

On the other hand, lithium stearate is that salt, for which the sum of the distribution exponents has the lowest value (—1.2). The alcoholic solution of this salt must be 4 times as concentrated as the aqueous solution, before distribution equilibrium between the solutions is established.

The figures in parenthesis in table 1 are especially uncertain.

By measuring *the electromotive force* of such a chain as

$$H_2 \mid HCl \text{ in water, AgCl} \mid Ag\text{—}Ag \mid AgCl, HCl \text{ in alcohol} \mid H_2,$$
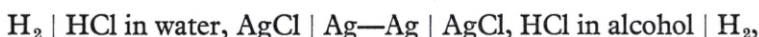
in which an element with aqueous electrolyte is combined against the same element with alcoholic electrolyte, it is also possible to determine sums of ion-distribution exponents. In this way, from Fleysher's electrometric measurements,

we have computed the sum of the distribution exponents of the hydrogen and chloride ion to 4.8.

For a weak acid one is able to compute the sum of the distribution exponents of the ions $(P_H + P_{anion})$ when the dissociation constants of the acid in the two media $(K_{H_2O}$ and $K_A)$ are known. As Larsson demonstrated in his doctor's thesis, we find:

$$P_H + P_{anion} - P_{undiss.\ acid} = \log K_{H_2O} - \log K_A = \Delta \log K.$$

It is therefore possible to determine the sum of the distribution exponents of the ions by adding the distribution exponent for the undissociated acid to the difference between the logarithms of the dissociation constants of the acids in the two media. This last distribution coefficient may be determined by means of the solubility of the acid in water and alcohol. This method is used in determining the distribution exponent of the ions of benzoic acid, salicylic acid, and the three nitrobenzoic acids (see table 2).

Table 2. The sum of the ion-distribution exponents between water and alcohol for different weak acids, calculated from the dissociation constants of the acids in water and in alcohol

Benzoic acid	3.91
Salicylic acid	3.47
o-Nitrobenzoic acid	4.25
m- — -	3.17
p- — -	3.33

It is of course of special interest to determine the *distribution exponents of the individual ions*. Larsson has attempted this in his doctor's thesis. It is known that *a saturated aqueous solution of potassium chloride* possesses only a very small diffusion potential against dilute aqueous solutions. He assumes that it also shows *a negligibly small potential against alcoholic solutions*. I shall discuss the justification of this assumption later.

By measuring the potential in a cell such as,

$$H_2 \mid HCl\ in\ H_2O \mid 3.5\ M\ KCl\ in\ H_2O \mid HCl\ in\ alcohol \mid H_2$$
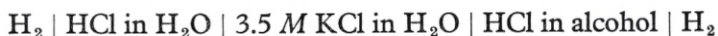
and using his above-mentioned assumption, Larsson computes the distribution exponent of the hydrogen ion to 2.52, and, in a similar way, that of the silver ion, the benzoate ion and the chloride ion to 2.06, 1.27, and 2.51, respectively. Continuing in the same way, we have computed the distribution exponent of the bromide ion to 1.84.

By means of these distribution exponents of the individual ions and our other material of distribution-exponent sums, it has been possible to list in table 3 a few ion-distribution exponents. The values vary from 4.1 for the potassium ion to —3.9 for the stearate ion.

Table 3. Distribution exponents of ions between water and alcohol

H+	2.5	Cl⁻		2.5
Li+	2.8	Br⁻		1.8
Na+	3.5	J⁻		1.4
K+	4.1	ClO₄⁻		0.7
Rb+	3.9	Benzoate ion		1.3
Cs+	4.0	Salicylate ion		1.2
Ag+	2.1	o-Nitrobenzoate ion		1.7
NH₄+	2.7	m-	—	0.7
N(CH₃)₄+	3.0	p-	—	0.8
N(C₂H₅)₄+	2.7	Laurate ion		—2.4
		Myristate ion		—3.5
		Palmitate ion		—3.7
		Stearate ion		—3.9

II

Roughly speaking, it may be said, that the way in which ions distribute themselves indicates that they prefer to be in water. Even though not all salts are soluble in water, yet they are almost all more soluble in water than in alcohol and in other non-aqueous solvents. This fact is the basis of the definition of salts by the ancient chemists as substances soluble in water.

The preference of ions for water is due to the large dielectric constant of that medium. When an electrically charged body is transferred from a dielectric to a vacuum, a certain (electric) work must be overcome. At the moment the body, for instance, is just above the surface of the dielectric, that surface will possess an opposite electric charge, and will therefore try to prevent the removal. Some years ago, Born showed that this work for a spherical z-valent ion, with radius r, may be expressed by $\dfrac{(z\varepsilon)^2}{2r}\left(1 - \dfrac{1}{D}\right)$ (ε denotes the charge of the electron and D the dielectric constant of the medium). He discovered, moreover, that this expression for reasonable values of r leads to plausible values for the development of heat by the transference of ions from vacuum into aqueous solution. Fajans had already earlier computed such *heats of solution* from experimental data and named them heats of hydration of the ions, a name, which to me seems somewhat misleading. Hückel followed the same principle in developing his formula for ion-activity coefficients in concentrated solutions, and also Scatchard has used this principle in his theory of the e. m. f. of cells with aqueous-alcoholic electrolytes.

Transferring a z-valent ion with radius r from water (with $D = 81$) to alcohol (with $D = 26$), the *electric work* to be overcome may be expressed as follows:

$$\frac{(z\varepsilon)^2}{2r}\left(\frac{1}{26} - \frac{1}{81}\right).$$

This electric work introduces in the distribution exponent between water and alcohol an electric term: $P_e = \dfrac{(z\varepsilon)^2}{2rKT} \log e \left(\dfrac{1}{26} - \dfrac{1}{81}\right)$ which when solved gives $P_e = 3.15 \dfrac{z^2}{r}$ (z denotes the valency and r the radius in Å of the ion). For mono-valent ions with radii 1, 2, and 3 Å, P_e is, respectively, 3.15, 1.6, and 1.05.

If the distribution exponent for the same atom group, when uncharged, is P_u, the distribution exponent P for the ion will be

$$P = P_e + P_u = 3.15 \frac{z^2}{r} + P_u.$$

As is well-known, ions like K^+ and Cl^- are supposed to possess an external electronic structure, similar to that of argon. Therefore the above formula could be tested by adding to the distribution exponent of argon between water and alcohol, the electric term P_e, and thus finding out whether, by that means, the distribution exponents of the potassium and the chloride ions were obtained. Unfortunately, in so far as I know, the solubility in alcohol of rare gases has not yet been measured, but we are now planning experiments along those lines.

If P is known for the entire series of rare gases, He, Ne, A, Kr, X, it may be possible to make a more exact calculation, by considering that K^+ and Cl^- are, respectively, a little smaller and a little larger than the argon atom, and, in calculating the non-electric part of the distribution exponents of the ions to interpolate between the distribution exponents of the rare gases.

For a larger organic ion, as for instance the benzoate ion, we may assume that the non-electric part is nearly the same as the entire value for the undissociated benzoic acid. Hence, we have

$$P(\text{benzoate}) = P_e + P(\text{benzoic acid}).$$

If this equation is combined with the previously mentioned equation from Larsson's thesis:

$$P_H + P(\text{benzoate}) - P(\text{benzoic acid}) = \Delta \log K,$$

we find,

$$P_H + P_e = \Delta \log K.$$

($\Delta \log K$ expresses the difference between the value of $\log K$ in water and in alcohol).

Heinrich Goldschmidt has found that $\Delta \log K$ is nearly constant for organic carboxylic acids. This agrees well with the above formula. According to Goldschmidt, $\Delta \log K =$ about 6. If we set $P_H = 2.5$, we find $P_e =$ about 3.5, corresponding to an effective radius for the carboxyl group of about 0.8 Å.

For phenols, $\Delta \log K$ is smaller than for carboxylic acids; P_e is therefore also smaller. The effective radius of the phenolate group is consequently larger. This may be explained by the location of the electric charge less close to the surface.

When we remember that the electric part of the distribution exponent of carboxylate ions is about 3.5, whereas the entire distribution exponent for a laurate ion is only —2.4 and that for a stearate ion is but —3.9, we see that the paraffine end of these ions reduces the distribution exponent with 5.9 and 7.4 respectively, a proof of the power with which the paraffine part of the molecule shuns water.

It is comprehensible that ions with so different reactions to water in their two ends, must energetically orientate themselves in the surface of an aqueous solution with the paraffine end outwards and the carboxyl end inwards; moreover, they must have a tendency to form aggregates, "micells", with the paraffine tails inwards, and the carboxyl ends outwards, towards the water.

The ability of soaps to lather, as well as their colloidal characteristics, may perhaps be approximately measured by the difference between the distribution exponents of their carboxyl ends $(= P_e)$ and their paraffine ends $(= P - P_e)$.

In the case of polyvalent ions, the electric term in the distribution exponent increases with the second power of the magnitude of the charge. Therefore, in the case of the di- and tri-valent ions, the difference between the solubility in water and in alcohol is, on the average, much larger than in the case of monovalent ions. In practice, this is illustrated by the difficulty that exists in finding salts with polyvalent ions, with even an appreciable solubility in alcohol.

Therefore, when salts are precipitated from aqueous solutions by the addition of alcohol, the solubility of salts with polyvalent ions decreases more rapidly under the addition of alcohol, than that of salts with monovalent ions.

In an other connection, Gjaldbæk has recently determined the solubility of three different salts in a series of mixtures of water and alcohol.

Table 4 shows his results which he communicated to me privately.

Table 4. The solubility of three different salts in alcohol of various strengths at about 22° C, according to Gjaldbæk

Strength of alcohol	Solubility in g. per l. saturated solution of:		
	NaCl uni-univalent	$Na_2S_4O_6,2H_2O$ uni-divalent	$Na_3Au (S_2O_3)_2,2H_2O$ uni-trivalent
50 % Tralles	114	382	77
60 – –	76	252	29
70 – –	45	160	8
80 – –	40	66	2
90 – –	4	10	0

The figures demonstrate clearly how the influence of the percentage of alcohol on the solubility increases with the valency of the ions. The very concentrated solutions of sodium tetrathionate in 50 per cent and 60 per cent alcohol shows this less clearly than the solutions of sodium chloride; however, in these strongly concentrated solutions, the activity of the ions increases undoubtedly much more rapidly than their concentration. The third salt is the complex sodium auro-thiosulphate containing the trivalent aurothiosulphate ion.

As a matter of fact, water is not a continuous dielectric, but an aggregate of dipole molecules. Therefore the formula for the electric part of the distribution exponent of an ion expressed by

$$P_e = \frac{z^2}{r} \, 3.15$$

is only approximate. The smaller the ion, the more uncertain the formula becomes. The orientation of the dipole molecules of the water around an ion assumes, when the ion is very small, the character of a chemical hydration, and Born's formula is certainly not applicable. This, for instance, is true of the hydrogen ion; this ion is present in water as H^+, H_2O and in alcohol as H^+, C_2H_5OH. In mixtures of water and alcohol it appears in both forms. In the theory of P, this must be taken into account.

In mixtures of water and alcohol, we have the following chemical equilibrium for the hydrogen ion

$$H^+, C_2H_5OH + H_2O \rightleftharpoons H^+, H_2O + C_2H_5OH$$

The equilibrium constant for this process has been determined by H. Goldschmidt. If we introduce molar concentrations of the ions and the vapour tensions of water and alcohol expressed in fractions of the vapour tensions of the pure liquids, we find $K =$ about 100 in solutions rich in alcohol.

It is possible to demonstrate that the gross distribution exponent P_H, which we, in the preceding, have computed without taking the solvation into account, may be expressed by the following equation

$$P_H = \log K + P(H^+, H_2O),$$

in which $P(H^+, H_2O)$ indicates the distribution coefficient of the hydrated ion. K varies, depending on whether the value of the equilibrium constant has been determined in alcohol containing a little water, or in water containing a little alcohol. It is the former value we must use. As previously stated, it is about 100. If we introduce this value of K we obtain for the distribution coefficient of the hydrated hydrogen ion the surprisingly small value 0.5. However this is supported by the fact that a similar small value seems to hold for the hydroxyl ion, which, considering the smallness of the hydrogen nucleus must be assumed to

resemble the hydrogen ion a great deal. As the formulae H_3O^+ and HO^- show, the difference between them is merely two hydrogen nuclei.

III

Knowledge about the ion-distribution coefficients is of value in many respects. With the help of these coefficients it is possible, when the solubility of a salt in one medium is known, to determine the solubility of the salt in other media, or, when the e.m.f. of a cell with one solvent is known, to calculate the e.m.f. of the same cell with other solvents.

Of special interest is the connection between the ion-distribution coefficient and the so-called *phase-boundary potentials*.

Between two immiscible media, which contain an electrolyte in distribution equilibrium, a phase-boundary potential always exists, provided the distribution exponents for the cation and anion, P_K and P_A, are not equal. Only by means of this potential is it possible to have distribution equilibrium with the same ratio of the concentrations of both cation and anion. The phase-boundary potential will influence the distribution of oppositely charged ions in opposite directions, and can thus make the distribution of the ions in equilibrium uniform, in spite of different distribution exponents.

This phase-boundary potential is (at 25° C and in the case of monovalent ions) expressed by the equation:

$$\pi_F = \tfrac{1}{2} \cdot 0.0591 \, (P_K - P_A)$$

The potential is independent of the mobility of the ions and is solely determined by their distribution exponents.

If the electrolyte is not in distribution equilibrium between the two phases, a diffusion from one phase into the other will take place. It is natural to assume that distribution equilibrium will most often occur at the phase boundary itself, and that the very phase-boundary potential will be determined by the above formula. To this is added the diffusion potentials π_D on both sides of the phase boundary, determined according to Nernst's formula from the mobilities of the ions. The following equation designates the entire phase potential:

$$\pi = \pi_D + \pi_F = \pi_D + \tfrac{1}{2} \cdot 0.0591 \, (P_K - P_A).$$

It is possible with some degree of approximation to use the same formula for the potential between salt solutions in two intermiscible media as water and alcohol. The entire potential is the sum of a *phase-boundary potential* which is determined by the distribution exponents of the ions, and *diffusion potentials* which depend on the mobilities of the ions, and which are the greater, the further the solutions are from being in distribution equilibrium with each other as regards the electrolyte.

We will use this theory in investigating the justification of assuming the potential between saturated aqueous KCl-solution and dilute alcoholic solutions to be zero.

Let us assume that the potential has the value x. Then the distribution exponent of the potassium ion, instead of 4.1 as computed earlier, will be $4.1 + \dfrac{x}{0.0591}$, and in a similar way for the chloride ion $2.5 - \dfrac{x}{0.0591}$. According to these formulae, the entire potential may be expressed by the equation

$$x = \frac{0.0591}{2} \left[4.1 + \frac{x}{0.0591} - \left(2.5 - \frac{x}{0.0591} \right) \right] + \pi_D$$

As is readily seen, x vanishes and the equation is simplified to

$$\tfrac{1}{2} \cdot 0.0591 \cdot 1.6 + \pi_D = 0$$

Let us first consider the fact that x vanishes. As a result of this, we are unable to say anything on the basis of our experiments about the absolute value of the phase-boundary potential, nor, indeed, anything about the absolute magnitude of the distribution exponents. Possibly P_K is larger (or smaller) than 4.1, but if this be the case, all distribution exponents of the cations are, likewise, just as much larger (or smaller) and all the distribution exponents of the anions just as much smaller (or larger).

Another conclusion may be drawn from the above equation. Accepting Larsson's assumption about the potential 0 between saturated aqueous potassium chloride solution and dilute alcoholic solutions, we find the distribution exponents for K^+ and Cl^- to have a difference of 1.6. This shows that π_D must equal $-\tfrac{1}{2} 0.0591 \cdot 1.6 = -0.047$ volts, and that therefore it was not permissible to ignore the diffusion potentials. The explanation for this must lie in the fact that the migration velocities of K^+ and Cl^- differ so much that the diffusion potentials in water and especially in alcohol are not negligible. For the present I have, however, refrained from correcting the given distribution coefficients, since, even after such a correction, the values would still be relative, as is described above, because we do not know the value of x.

However, certain considerations indicate that the distribution exponents of individual ions shown in table 3, are not far from being correct. Theoretically, it is most probable that the distribution exponent of the large chloride ion will be smaller than that of the structurally similar, smaller potassium ion, just as the values, 2.5 and 4.1, in table 3, show. Therefore Larsson's assumption, that the potential difference between a saturated, aqueous potassium chloride solution and a dilute alcoholic solution is equal to zero, is also, perhaps, not far from the truth.

9

If *the temperature of a medium changes*, it may be considered a different medium. We may therefore speak of distribution coefficients between water of 25° C and water of 75° C. It is this kind of thermal distribution coefficients, which Soret, in his days, determined by placing the salt solution in a vertical tube and keeping the upper end of the tube at a higher temperature for a considerable time, and then analyzing the solution at the top and at the bottom of the tube. As found by van't Hoff and Arrhenius, it is impossible to explain Soret's experiment by merely taking into account the change in osmotic pressure with temperature. Other forces must be at work, and based on the above, the change in the dielectric constant of the water must produce one such force. We have found, however, that for the present, it is not enough to take this force into consideration, though certain main lines in the experimental results of Soret's effect may be explained in this way, especially the fact that it is electrolytes with polyvalent ions (as $CuSO_4$) which show strong Soret effects.

Because of the different distribution coefficients of the ions between cold and hot water, and their different migration velocities, *thermo-electric forces* must arise when one end of a salt solution is heated. Nernst and his pupils have studied these electromotive forces. Their investigations show that special forces come into play here, too. Both in Soret's phenomenon and in the thermo-electric forces arising in electrolyte solutions of different temperature, there are possibilities for experimental investigations, which will give us information about ion-distribution coefficients.

As I hope I have made plain in the above, the ion-distribution coefficients are figures which procure us a comprehensive survey of a series of very different properties of electrolyte solutions. In the theory of ion-distribution coefficients advanced here, we have a theory applicable to all these properties. This theory leads us an essential step closer to the solution of the important problem of calculating in advance the solubility of salts in water and other solvents.

For the further development and extension of the theory, a considerable increase of the available experimental material is, however, necessary. It is to be hoped that such material will be at hand in the years which lie just ahead.

This lecture is, in the main, based on a paper in which Dr. E. Larsson, Lund, was my collaborator, and which is not yet published.