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On the Theory of the Distribution of Electrolytes Between a Solid Crystalline and a Liquid Phase

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A short discussion of the nature of distribution equilibria between mixed crystals and aqueous solutions is given. From the general theory of the thermodynamical potential and the activity theory of strong electrolytes, equations are deduced giving the influence of the composition of the liquid phase on the distribution ratio and the dependence

of the partition constant on the properties of the pure components. The relative importance of the various factors in these equations, depending on the concentrations and properties of the components, is discussed. The deduced equations are in agreement with the experimental data.

THE conception of solid solution was first introduced into science by J. H. van't Hoff in the year 1890.¹ In support of such a view of solid mixtures he had already pointed out the distribution between solid and liquid solutions. If solid mixtures are really solutions the distribution of a substance between a solid and a liquid phase must take place according to the Berthelot-Nernst distribution law— $C_s/C_L = K_N$, where C_s and C_L are the concentrations of the micro-component in the solid and liquid phases, respectively, in case the following three requirements are fulfilled: (1) the solutions must be dilute enough with respect to the distributing substance in order that the variations in its content do not affect the thermodynamic properties of the solutions; (2) true equilibrium between phases and throughout each phase must be attained; and (3) the distributing substance must be in the same molecular state in both phases.

Since then a great number of investigations have been published concerning the question, but with very discordant results.² The cause of the discrepancies lie in the difficulty of attaining equilibrium, because of the extreme slowness of diffusion in crystals at ordinary temperatures; for the same reason inhomogeneous crystals once

formed "freeze in" and do not spontaneously become uniform. Many investigators have paid much attention to this circumstance and have even considered the equilibrium conception, as well as the thermodynamical laws, inapplicable to the crystalline mixtures.³

But thermodynamics is not bound to any particular mechanism that fulfills its requirements. Diffusion is only a very convenient method for attaining equilibrium and does not affect the fundamental thermodynamical properties such as internal energy, entropy, etc. Therefore it is clear that the practical absence of diffusion in crystals at ordinary temperatures is only a matter of experimental method of attaining equilibrium and not of the inapplicability in principle of thermodynamics to the crystalline mixtures.

In fact in recent years Professor V. Chlopin and his collaborators⁴ have worked out several methods of attaining equilibrium between mixed crystals and solutions, based on the recrystallization phenomenon. During the process of recrystallization each molecule of salt passes many times through the solution and, if this process is repeated often enough, an equilibrium between crystals and solution is established, and all the resulting crystals grow up from a solution of constant composition. Such crystals are quite homogeneous, and the Berthelot-Nernst distri-

¹ J. H. van't Hoff, *Zeits. f. physik. Chemie* **5**, 322 (1890).

² G. Bruni, *Feste Lösungen und Isomorphismus*, Leipzig, 1908, where the early literature is given. See also G. Tammann, *Zeits. f. anorg. Chemie* **87**, 1 (1919); G. Tammann and A. Svorykin, *Zeits. f. anorg. Chemie* **173**, 75 (1928); G. Meyer, *Rec. Trav. Chim. Pays-Bas* **42**, 304 (1923).

³ See Tammann, reference 2.

⁴ For a summary see: V. Chlopin, A. Polessitsky, A. Ratner and P. Tolmatscheff, *Ber.* **64**, 2653 (1931); see also R. Mumbrauer, *Zeits. f. physik. Chemie* **A156**, 113 (1931).

bution law is strictly valid for them. The true character of equilibrium attained is proved by the fact that the value of the distribution constant is the same independently of the side from which the equilibrium is attained, i.e., whether the distributing salt (usually a radioelement in concentrations of the order of 10^{-10} mol./cc) was added to the solution, or to the crystals at the beginning. The same result may be attained also more conveniently, especially at ordinary temperatures, by means of a rapid crystallization from a supersaturated solution with powerful stirring. Under such conditions, the recrystallization of minute crystals goes on very fast, and the equilibrium is reached in the process of growth of the crystals from the submicroscopical dimensions. In order to attain the equilibrium by crystallization from a supersaturated solution without such stirring, the crystallization must take place very slowly for otherwise instead of the simple form of the distribution law, the differential form or the so-called Doerner-Hoskins formula is followed. This formula is $\ln x = \lambda \ln y$, where x and y are the percents of the micro and macrocomponents, respectively, remaining in the solution. In that case, the concentration ratio remains constant for each surface layer of the growing crystals, but not for the crystal, as a whole. The same formula holds also for crystallization by slow evaporation, but the value of λ varies depending on the rate of evaporation and stirring, reaching, when the latter is good enough, the value of the partition factor $D = K_N C_L' / d$, where K_N is defined as above, and C_L' is the concentration of the macrocomponent in its saturated liquid solution.

These experiments have shown the possibility of attainment of an equilibrium state between a solid and a liquid solution, and have furnished a basis for further theoretical treatment of this subject. Such treatment is required in the first place in order to find the influence of the composition of phases on the value of the distribution constant. Such an influence was found experimentally by Professor V. Chlopin and his co-workers,⁵ but the relations are too complicated to be made clear by purely experimental methods.

⁵ V. Chlopin and A. Polessitsky, *Zeits. f. physik. Chemie* **A145**, 57 (1929); V. Chlopin and A. Ratner, *Comptes Rendus Acad. Sciences U. S. S. R.* 723 (1930).

Since the work of van't Hoff and Roozeboom,⁶ the question has not been subjected to theoretical treatment, except in two works, one by K. Herzfeld on thermodynamics of the formation of mixed crystals⁷ and the other by L. Imre on the absorption view of the distribution.⁸

In the first work for which the distribution was only of secondary importance, the influence of the activity coefficients, so important in concentrated salt solutions, were lost sight of completely. Also the equation obtained is very complicated, because of the correction terms which have no importance for the distribution phenomena.

The second work deals only with the cases where the Doerner-Hoskins equation is valid, and L. Imre thinks, that in this case we are dealing with quite another phenomenon than the distribution attained by recrystallization, and that, due to the greater speed of the process, the adsorption equilibrium "freezes in" and that the work of "building on" (Anlagerung) and not that of "building into" (Einlagerung) is the more important. But these assumptions seem not to be true, for the range of rates of crystallization is the same for both cases. Which of the two forms of the distribution law holds depends not on the rate of crystallization, but on other conditions? If the number of crystals finally present is small compared with the number of crystallization centers originally formed, the crystals are homogeneous and the simple form of the distribution law is valid. But if the number of crystals is in the main the same during the entire process of crystallization, as in the evaporation experiments, or if their number diminishes by binding together of subcrystallites, and not by repeated recrystallization, the differential form of the distribution law holds, and if diffusion is eliminated, the value of λ is the same as that of the partition factor D . When the crystallization takes place without stirring, the equilibrium is not attained due to the slowness of diffusion and the observed values of λ lie nearer to 1 than corresponding values of D . Thus we have no reason to use different laws for different cases of crystallization and to take into account

⁶ B. Roozeboom, *Zeits. f. physik. Chemie* **8**, 504 (1891).

⁷ K. Herzfeld, *Zeits. f. Physik* **16**, 84 (1923).

⁸ L. Imre, *Zeits. f. physik. Chemie* **A164**, 364 (1933).

the work of "building on" instead of "building into" even when the Doerner-Hoskins formula is followed. L. Imre himself takes as the base of his calculation the values of heat of solution of the components when calculating the value of λ from his equation. But the heat of solution corresponds to the work of bringing the salt into the solution from the volume of the crystal and not from its surface, in other words, to the work of "building into" and not of "building on." Obviously the right order of the value found for λ based on those heats of solution speaks against L. Imre's ideas of "freezing in" of absorption equilibrium rather than for them. Because of these considerations I took as a starting point for my work the thermodynamical treatment of the equilibrium state based on the general theory of chemical potentials and on modern activity theory of strong electrolytes and not the kinetics of crystallization. This allowed me to find definite connections between the value of D , the composition of the solution and the properties of the pure components.

THEORETICAL PART

Notation

In this work the following notations are used: x = mol fraction; c = concentration in grams per liter; m = molality; L = solubility product; a_+ , a_- = activities of the ions; a = activity of the electrolyte as a whole = $a_+^{v+} a_-^{v-}$; γ_+ , γ_- = activity coefficients of the ions; γ = activity coefficient of the electrolyte; μ = Gibbs's chemical potential; \mathbf{u} = chemical potential in the standard state chosen in the usual way for a solute;⁹ d = specific weight of the crystals; D = partition factor = $K_N C' / d = C_s C' / C_L d$. The subscripts s and L refer to solid and liquid phases, respectively. The superscript ' refers to the macrocomponents.

DEDUCTION OF THE FORMULAE

According to the main statements of the theory of the chemical potential its value for the distributing substance at equilibrium must be the same in both phases:

$$\mu_L = \mathbf{u}_L + RT \ln a = \mu_s. \quad (1)$$

⁹ Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., New York, 1923, p. 259.

As in the solid phase we have a very dilute solution we can write for μ_s

$$\mu_s = \mathbf{u}_s + RT \ln x_s^{v+}. \quad (2)$$

The x_s^{v-} is omitted for the anion is common for both components and the only one in crystals. From (1) and (2) we obtain:

$$\ln (x_s^{v+} / a_+^{v+} a_-^{v-}) = (\mathbf{u}_L - \mathbf{u}_s) / RT. \quad (3)$$

For the saturated solution of the microcomponent in pure water, we can write

$$\mu_{0s} = \mathbf{u}_L + RT \ln a_0. \quad (4)$$

Substituting \mathbf{u}_L in (3) from (4) we obtain finally:

$$x_s^{v+} / a_+^{v+} a_-^{v-} = (1/a_0) e^{(\mu_{0s} - \mu_s) / RT}. \quad (5)$$

The right-hand side of this equation does not depend on the composition of the liquid phase; therefore we have in it the main expression for the distribution constant of an electrolyte between a solid and a liquid phase.

For the most important case practically, i.e., when the solid phase is a pure salt isomorphous with the microcomponent, the Eq. (5) can be transformed into another form more convenient for comparison with experiment. This may be done by multiplication of both sides of the Eq. (5) by the activity of the microcomponent, the same in all the solutions and equal to a_0 , the activity in pure saturated solution since they are all in equilibrium with the pure solid macrocomponent. Taking into account that a_-' and a_- is the same quantity, for it refers to a common ion in a common solution, and expressing the activities through molalities, we obtain:

$$\frac{x_s^{v+} m_+^{v+} \gamma_+^{v+}}{m_+^{v+} \gamma_+^{v+} a_0} = \frac{a_0'}{a_0} e^{(\mu_{0s} - \mu_s) / RT} = D_0. \quad (6)$$

The quantity D_0 may be called the "true partition constant," for on one hand, it does not depend on the composition of the liquid phase and on the other hand it is connected with the partition factor D , which is usually employed to express the experimental results, and as a characteristic of the course of the fractional crystallization. We can divide the Eq. (6) into two:

$$\frac{x_s^{v+} m_+^{v+} \gamma_+^{v+}}{m_+^{v+} \gamma_+^{v+}} = D_0 \quad (6a)$$

and

$$D_0 = (a_0'/a_0)e^{(\mu_{0s}-\mu_s)/RT}, \quad (6b)$$

the first of which expresses the dependence of the concentrations of the components in both phases on one another, and the second the dependence of the value of D_0 upon the properties of the pure components.

DISCUSSION OF THE RESULTS

The left-hand side of Eq. (6a) consists of two factors: $x_s^{\nu_+}m_+^{\nu_+}/m_+^{\nu_+}$ represents the law of distribution of an electrolyte as it would be if the solutions were ideal, and the second $\gamma_+^{\nu_+}/\gamma_+^{\nu_+}$ containing the activity coefficients, gives the correction due to deviations of the solutions from ideal. We can see from it, that in ideal or very dilute solutions the first term must be constant regardless of the composition changes of the solution. For the case $\nu_+=1$, as in all hitherto studied systems, the first factor becomes identical with the partition factor D .

Up till now in all the works on the distribution of radioelements, between solid and liquid phases, it was admitted, that because of the very minute concentrations used (of the order of 10^{-10} mol/cc or even less) we can consider their solutions as ideal and neglect the activity coefficients. But that supposition is only partly true; namely, in that the variations in the content of the radioelements do not influence the activity coefficients of the components, and this is the reason for good constancy of the partition factor at constant composition of the solution obtained. But as the activity coefficient of an electrolyte depends on the total ionic strength of the solution and not upon the concentration of the given electrolyte, and we usually deal with more or less concentrated salt solutions, the γ_+ is very far from unity and depends very much on the composition of the liquid phase.

But, as it is seen from the Eq. (6a) the second factor consists not of γ_+ only, but of the ratio $\gamma_+^{\nu_+}/\gamma_+$, and that ratio can be considered as equal to unity, or at least as independent of the composition in a limited range, even in fairly concentrated solutions, for the ions of the components are of the same valency and do not differ very much in dimensions for otherwise they could not form isomorphous crystals.

The range of the probable constancy of D becomes even larger if we take into consideration that γ_+ of the Eq. (6a) is the activity coefficient of the microcomponent when added to the solution of the macrocomponent and not in a solution of the same concentration of itself only. As some of the factors that determine the deviations of the behavior of electrolytes from the ideal depend on all the ions in solution (electric field in the solution, dielectric constant) and some upon the particular ion under consideration (polarizability, degree of ionization, side chemical reactions) we may expect that generally the value of the activity coefficient of an ion, when added to a much larger quantity of another ion would lie nearer to the value of γ for the latter at the same ionic strength, than the value of pure microcomponent.¹⁰ Also, the changes of the activity coefficient of microcomponent in such solutions lie nearer to the corresponding changes of the activity coefficient of the macrocomponent than they would to such changes in a pure solution of the microcomponent. Obviously the difference of the behavior of the components must be the smaller, and the constancy of the ratio of the γ 's the better, the more dilute the solution is and the more alike the ions of the components are.

Turning now to the comparison of the Eq. (6a) with the experimental data, we meet with the lack of knowledge of the activity coefficients in such mixed solutions. But the above considerations show a way for approximate proof of this equation, namely, by taking D instead of D_0 and comparing then the deviations from constancy caused by this substitution with what may be expected from the electrochemical properties of the components.

In the Tables I, II and III are collected all the available data on the variation of the distribution constant with the composition of the liquid phase.

¹⁰ So it is generally, but not always for the above factors change the activity coefficients in different directions, and we may find sometimes that as a result of their interaction the activity coefficient of the microcomponent would get farther from that of macrocomponent instead of approaching it. Such is the case for HCl in concentrated solutions of LiCl (see J. Hawkins, J. Am. Chem. Soc. **54**, 4480 (1932).

TABLE I. $Pb(NO_3)_2-Ra(NO_3)_2$ at 25° .*

Composition of the solution		K_N	D
1.82 m $Pb(NO_3)_2$		18.2	2.19
1.01 " "	1.09 m HNO_3	41.9	2.81
4.55 " "	$\left\{ \begin{array}{l} 7.12 \text{ " } NaC_2H_3O_2 \\ 3.29 \text{ " } HC_2H_3O_2 \end{array} \right\}$	26.3	4.55

* V. Chlopin and A. Ratner, reference 5.

TABLE II. $BaBr_2-RaBr_2$ at 0° .*

Composition of the solution		K_N	D
3.11 m $BaBr_2$		52.8	12.4
2.92 " "	0.27 m HBr	57.7	13.2
2.84 " "	0.43 " "	59.1	12.8
2.67 " "	0.64 " "	58.3	11.9
2.42 " "	1.03 " "	68.4	12.6
1.72 " "	2.22 " "	116.0	15.4
1.27 " "	2.92 " "	146.0	14.2
0.74 " "	4.00 " "	173.4	9.8
0.42 " "	4.81 " "	243.0	7.8

* V. Chlopin and B. Nikitin, Zeits. f. anorg. Chemie **166**, 311 (1927).TABLE III. $Ba(NO_3)_2-Ra(NO_3)_2$.*

Composition of the solution		t°	K_N	D
0.411 m $Ba(NO_3)_2$		25°	46.0	1.49
0.367 " "	0.530 m $BaCl_2$	"	21.7	1.56
0.195 " "	0.585 " HNO_3	"	85.2	1.31
0.674 " "	$\left\{ \begin{array}{l} 3.34 \text{ " } NaC_2H_3O_2 \\ 0.13 \text{ " } HC_2H_3O_2 \end{array} \right\}$	"	25.5	1.34
0.400 " "	0.209 " $HgCl_2$	"	44.7	1.39
0.416 " "	1.18 " glucose	"	56.1	1.60
0.189 " "		0°	154.0	2.31
0.080 " "	0.423 " HNO_3	"	334.0	2.12
0.185 " "	0.202 " $BaCl_2$	"	64.0	2.24

* V. Chlopin, A. Ratner and P. Tolmatscheff, unpublished.

As it may be seen from the tables, the constancy of D is in full accord with the above considerations, the worst in the case of lead nitrate as macrocomponent, because of the large solubility of lead nitrate and the great difference in properties between lead and radium ions and the best for the sparingly soluble barium nitrate whose cation is very much more similar to the radium ion. In the last case the constancy of D is fairly good (within 20 percent) though the K_N values vary many times.

But not only the degree of constancy of D , but also the direction of deviations from it is in full accord with what could be expected from the properties of the components. Thus in the

case of lead nitrate which is much more associated electrolytically than barium and radium salts¹¹ and gives nondissociated basic acetates on addition of HNO_3 or $NaC_2H_3O_2$ the activity coefficient of lead γ_+ falls a great deal faster than that of radium, the ratio γ_+'/γ_+ falls too, and as D_0 must remain constant, D must rise, which is the case. For barium salts the conditions are reversed, for radium salts must be more associated than those of barium because of the larger polarizability of radium, and we see in Tables II and III that D in these systems decreases slightly but systematically in all cases on addition of corresponding acids. So it seems that the Eq. (6a) is wholly confirmed by the experiment.

Expressing the activities through molalities, we can write Eq. (6b)

$$D_0 = (L_0'/L_0)(\gamma_0'/\gamma_0)e^{(\mu_{0s}-\mu_s)/RT}.$$

The first factor on the right-hand side of this equation, which would have been the only one if both phases were ideal mixtures, gives the connection between the partition factor and the solubilities of the components. The existence of such a connection was admitted by all chemists who had worked with the fractional crystallization and it was thought to be so direct that conclusions in regard to the identity of the solubility of the components¹² were made from an unsuccessful attempt of fractional crystallization. But an exact investigation, experimental or theoretical, on the existence and form of such a connection was still lacking, and in recent years there has been accumulated material contradicting it, at least in such exact form as it was assumed before.¹³

It follows from Eq. (6b) that this connection consists of a proportionality to the ratio of the solubility products but is masked by the influence of the non-ideal behavior of the solutions expressed in the liquid by the activity coefficients, and for the solid in the term $e^{(\mu_{0s}-\mu_s)/RT}$. These influences, especially that of the liquid phase,

¹¹ Plake, Zeits. f. physik. Chemie **A162**, 24 (1932).¹² M. Curie, *Traite de Radioactive*, Gauthier, Villard, Paris, 1910. V.I. p. 174.¹³ V. Chlopin, Zeits. f. anorg. Chemie **143**, 97 (1923); O. E. Erbacher, Ber. **63**, 141 (1930); A. Polesitsky, Zeits. f. physik. Chemie **A161**, 325 (1932).

may change the value of D_0 many times and thus the above-mentioned experimental facts are explained.

The comparison of the Eq. (6b) with experiment is even more difficult than that of Eq. (6a) for we meet again with the absence of data for the ratio γ_+'/γ_+ , but here we need the constancy of that ratio as well as its absolute value. Further the term $e^{(\mu_{0s}-\mu_s)/RT}$ is also undeterminable as yet, for the theoretical calculation of lattice energies is not exact enough and its computation from the heats of solution of the mixed crystals also fails because of the absence of such determinations through a sufficiently large range of concentrations. We could pass over all these difficulties by means of a determination of the partition constant for a weakly soluble macrocomponent at different temperatures, but even with data now available we can judge of the validity of the Eq. (6b) by comparing the values of D with the ratios a_0'/a_0 for all the systems, for which the solubilities of the components are known.

These data for $t=20^\circ\text{C}$ are given in Table IV in the first column of which the systems considered are given, the microcomponent being placed in brackets. The solubilities of radium salts are taken from the work of O. Erbacher,¹⁴ and the values of activity coefficients necessary

for the figures of the fourth column were evaluated approximately by a graphical extrapolation, using Lucass'¹⁵ data on alkaline earths chlorides for the halide systems, and Gellbach and Heppke's¹⁶ on barium bromide, and the author's determinations at 70° on the nitrates (by vapor pressure methods, unpublished).

From Table IV we see that the partition factors show an unmistakable parallelism to the activity ratios, though they are by no means equal to the theoretical values, the discrepancy increasing with increased solubility of the macrocomponent. At the same time, it is difficult to speak even of a parallelism between the solubility ratios and the partition factors.

We may go slightly further for the system $\text{Ba(Pb)(NO}_3)_2$ due to the determination of the heats of solution of mixed crystals of barium and lead nitrates made by G. Tamman,¹⁷ which enables us to compute at least the sign and order of magnitude of $\mu_{0s}-\mu_s$. This computation gives the value of 400–600 cal., from which

$$D_0 = a_0'/a_0 e^{(\mu_{0s}-\mu_s)/RT} = 0.30.$$

The γ_+'/γ_+ for this system is equal approximately to 1.30 and the experimental value of D_0 is approximately 0.20. The agreement between these values may be considered as quite satisfactory, taking into account the very approximate character of the calculations.

At this point I wish to take the opportunity to acknowledge my gratitude to Professor V. Chlopin for his advice and continued attention throughout this work.

¹⁵ Lucass, J. Am. Chem. Soc. **47**, 743 (1925).

¹⁶ Gellbach and Heppke, J. Am. Chem. Soc. **48**, 1504 (1926).

¹⁷ G. Tamman and Krings, Zeits. f. anorg. Chemie **130**, 229 (1923).

TABLE IV.

System	m_0	m'_0/m_0	a'_0/a_0	D
Ba(Ra)Br ₂	3.50	1.91	60	11
Ba(Ra)Cl ₂	1.71	2.07	16.5	4.5
Ba(Ra)(NO ₃) ₂	0.33	0.83	1.14	1.6
Ba(Pb)(NO ₃) ₂	0.33	0.20	0.12	0.16
Pb(Ra)(NO ₃) ₂	1.66	4.15	11.9	2.5
Pb(Ba)(NO ₃) ₂	1.66	5.03	8.32	2.4

¹⁴ O. Erbacher, Ber. **63**, 141 (1930).