ride, phosphorus trichloride, and hydrogen chloride are well established and the data obtained for these compounds prepared in the present study (Table III) checked very well with those reported in the literature.

Summary

When heated to about 500°, mixtures of P_2O_5 with simple fluorides or chlorides yielded POX_3 ($X = F$ or Cl) as the major volatile compound. PX_5 was not found in any case. In iron reaction vessels some PX_3 was formed due to reduction of POX_3 by the iron vessel. Mixtures of CaF_2 and NaCl with P_2O_5 yielded a mixture of PF_3, POF_3, POF_2Cl, $POFCl_2$, and $POCl_3$ upon heating to 350° or above. The reaction of P_2O_5 with rock phosphate and with fluorapatite at about 700° yielded some PF_3 and POF_3.

The melting and boiling points for POF_3 and PF_3 were determined, and vapor pressure equations calculated. The heats of sublimation, fusion and vaporization of POF_3, the heat of vaporization of PF_3, and Trouton's constant for both POF_3 and PF_3 were calculated. Difluophosphoric acid, HPO_2F_2, a new compound, was isolated. Carbon was found to reduce POF_3 to PF_3 at elevated temperatures.

The digestion of samples of PF_3 and POF_3 with concentrated $HClO_4$ was found to be convenient and satisfactory for converting the phosphorus to the orthophosphate ion for analysis. An analytical method was not found for determining the quantities of PF_3 and POF_3 in mixtures of the two compounds.

WILSON DAM, ALABAMA RECEIVED APRIL 25, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LINGNAN UNIVERSITY*]

Local Dielectric Constant and Solute Activity. A Hydration-Association Model for Strong Electrolytes

BY HENRY S. FRANK

Introduction

It has been shown recently[1] that the entropies of dilution of a number of strong electrolytes in aqueous solution show a general type of concentration dependence which can be plausibly interpreted on the basis of a few simple assumptions. One of these is that the ions affect the entropy of the solution in part through breaking down the structure of the water, and that the individual differences among the curves for different solutes are related chiefly to the different ways in which the ions exert this structure-breaking influence.

There seems to be no straight-forward general way to formulate the influence of the structure of a solution upon its thermodynamic properties. Since, however, a change in structure may be expected to have an effect on the dielectric constant, the influence through the dielectric constant on, say, the activity coefficient of a solute salt, will be one sort of contribution to the more general phenomenon. Since the local dielectric constant in the neighborhood of an ion is the quantity directly influenced by the structure effect of the ion, we shall want, in the first instance, to discuss the way in which a change in this local dielectric constant affects the activity coefficient of the solute ions.

A basis for this discussion has been given by Debye and Pauling.[2] For the purpose of showing that the validity of the limiting law of Debye and Hückel[3] is not impaired by changes in the dielectric constant around the central ion, they set up equations (see below) for the potential in two separate regions of different dielectric constant, with appropriate boundary conditions, and obtained a complicated expression for the potential of the central ion in its ion cloud. By expanding this expression in powers of concentration they showed that the leading term is exactly that given by the limiting law. They did not examine further the functional form of their expression, nor did they form any estimate of the magnitude of the deviations from the limiting law which their theory predicts. It is in these questions that we are at present interested. Before taking them up, however, we wish to consider an alternative derivation of the Debye-Pauling equation.

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* The Lingnan University is in Canton, China. It is at present operating partly in Canton and partly in Hong Kong at the University of Hong Kong. The trustees wish to state that the University's plant is undamaged and that its valuable work is being continued.

(1) H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, **8**, 933 (1940).

(2) P. Debye and L. Pauling, THIS JOURNAL, **47**, 2129 (1925).

(3) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

The Derivation of the Debye–Pauling Expression by the Integration of Energy Density.—It is well known in the theory of dielectrics that the electrostatic energy of a system can be represented as residing in the dielectric medium. It is also well known that such electrostatic energy is free energy, *i. e.*, its isothermal increment is equal to the reversible work done on the system, and its temperature derivative is in the negative entropy. In so far, therefore, as the Debye–Hückel (or the Debye–Pauling) theory is an internally consistent electrostatic theory in which the medium is pictured as a continuous dielectric, we should be able to derive the free energy of a central ion in its ion cloud by integrating the appropriate energy density expression over the space (filled with medium) surrounding the ion. Such a formulation should have special advantages for discussing problems related to entropy since, clearly, the causes of most of the entropy changes in electrolytic solutions are changes taking place in the aqueous medium, and a treatment of this sort makes it possible to identify the changes associated with a given region. A derivation along these lines is in fact possible, and is outlined herewith.

The fundamental assumptions are those of Debye and Pauling,[2] and are as follows. The ion is regarded as a sphere with a surface at a distance $r = a$ from the center (Fig. 1), this being the boundary between the ion proper and the external field, *i. e.*, the boundary inside which no other charges can penetrate. The charge ze is assumed to be located at the center of the ion. The dielectric constant within the ion, as well as outside of it to a distance $r = R$ (region I) is taken equal to D_1. The spherical shell of radius $r = R$ is assumed to be the site of a discontinuous change in dielectric constant, which is taken equal to D_2 from $r = R$ to $r = \infty$ (region II).

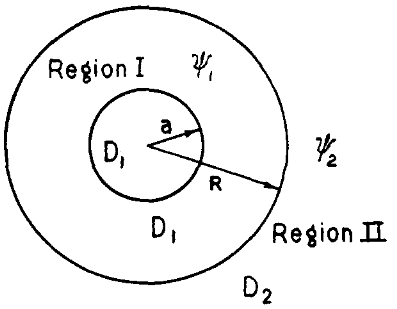

Fig. 1.—The Debye–Pauling model.

With these assumptions, the expressions for the potential ψ in each region are used as set up by Debye and Pauling.[2] The boundary conditions

$$\begin{array}{ll} \psi_2 \longrightarrow 0 & \text{as } r \longrightarrow \infty \\ \psi_1 = \psi_2 & \text{at } r = R \\ D_1 \dfrac{\mathrm{d}\psi_1}{\mathrm{d}r} = D_2 \dfrac{\mathrm{d}\psi_2}{\mathrm{d}r} & \text{at } r = R \\ D_1 \dfrac{\mathrm{d}\psi_1}{\mathrm{d}r} = -\dfrac{Ze}{r^2} & \text{at } r = a \end{array} \tag{1}$$

enable the constants of integration in ψ_1 and ψ_2 to be determined. Now from the electric force $E = -\mathrm{d}\psi/\mathrm{d}r$ in each region, the total (free) energy density $\mathrm{d}F/\mathrm{d}v$ at any point can be written

$$\frac{\mathrm{d}F}{\mathrm{d}v} = \frac{E^2D}{8\pi}$$

From this must be subtracted the contributions corresponding to the self-energy of the central ion and to the self-energy of the continuous distribution of electricity in the ion cloud. When this is done and the remainder integrated from $r = a$ to $r = R$ for region I, and from $r = R$ to $r = \infty$ for region II, there results an expression for F_D, the free energy of the central ion due to the presence of the ion cloud

$$F_D = \frac{Z^2e^2}{2D_1R} - \frac{Z^2e^2}{2D_2R} - \frac{Z^2e^2\lambda}{2D_1\delta_1}\,\frac{1 + \beta E}{1 + \dfrac{\lambda a}{\delta_1} - \left(1 - \dfrac{\lambda a}{\delta_1}\right)\beta E} \tag{2}$$

Where

$$\lambda \equiv \frac{4\pi e^2}{KT}\,\Sigma n_i Z_i^2$$

$\delta = \sqrt{D}$ (so that λ/δ for either region is the Debye–Hückel κ for that region); $E = e^{(2\lambda/\delta_1)(a - R)}$ and

$$\beta = \frac{1 + \dfrac{\lambda R}{\delta_2 + \delta_1}}{1 + \dfrac{\lambda R}{\delta_2 - \delta_1}}$$

For the ordinary Debye–Hückel case, $D_1 = D_2$, and

$$F_D = \frac{-Z^2e^2\kappa}{2D(1 + \kappa a)} \tag{3}$$

which is the classical result. The activity coefficient of the ion species under consideration can be obtained by multiplying F_D by Avogadro's number and equating the resulting quantity to the non-ideal partial molal free energy. This corresponds with the Güntelberg charging process[4] rather than the Debye process,[5] which could not be used here and for which, in order to obtain this result, it is necessary to neglect some terms.

Equation (3) can, of course, be derived with far less effort by making the simplification $D_1 =$

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(4) See N. Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

(5) P. Debye, *Physik. Z.*, **25**, 97 (1924).

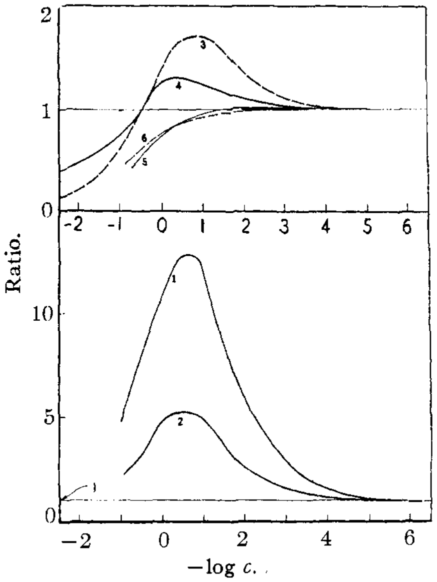

Fig. 2.—Ratio of F_D to limiting law value, as a function of log c, c in moles/liter: Curve 1, $D_1 = 4$, $a = 2$ Å., $R = 5$ Å.; curve 2, $D_1 = 4$, $a = 3$, $R = 5$; curve 3, $D_1 = 25$, $a = 3$, $R = 10$; curve 4, $D_1 = 25$, $a = 2$, $R = 5$; curve 5, $D_1 = 49$, $a = 3$, $R = 10$; curve 6, $D_1 = 25$, $a = 3$, $R = 5$.

D_2 at the outset. In this case the integration is from $r = a$ to $r = \infty$, and the integration constant in the potential expression has the value appropriate to the Debye–Hückel "first approximation." When this constant is given the "limiting law" value, and the integration is carried out from $r = 0$ to $r = \infty$, the limiting law expression $F_D = -z^2e^2\kappa/2\,D$ is obtained.

The only real difference between the equation (2) here obtained and that given by Debye and Pauling is that their expression is for the potential of the central ion instead of for its free energy, and it can be shown that after multiplication with $^1/_2ze$ their expression is identical with that of equation (2), in spite of the great difference in form. It is therefore necessary, and it is found to be true, that when (2) is expanded by developing β and E in series according to powers of λ, the first term is $-Z^2e^2\ \lambda/2D_2\delta_2$. An attempt to extend the study by retaining higher terms in this expansion encountered the difficulty, however, that the coefficients are large and alternate in sign so that no term-by-term analysis is possible. The alternative device was therefore adopted of assuming values for D_1, D_2, R, and a, and obtaining curves of F_D against c numerically. The results of such calculations are shown in Table I, and in Figs. 2 and 3. The values assumed for D_1, a, and R are shown in each case. D_2 was taken as 78.54 throughout, corresponding to a temperature of 25°. In Fig. 2, F_D is shown as a multiple of the limiting law value for the corresponding concentration, and $-\log c$ is used as abscissa to facilitate comparisons at the high dilutions at which important deviations occur. In Fig. 3 F_D is plotted against $\sqrt{c}$ for more conventional comparison with the limiting law. In view of the relation pointed out above between F_D and the partial molal free energy of the ion, the simple assumption that some sort of average values of a and R can be taken for positive and negative ions enables these curves to be interpreted in terms of log $\gamma_\pm$ for comparison with experimental findings. Another comparison with conventional theory is given by the values listed in Table I of a_{eff}. This quantity is defined by $F_D = -z^2e^2\,\kappa/(2D\ (1 + \kappa a_{\text{eff}}))$, and is the value a would have to have in a system of uniform dielectric constant to give the corresponding value of F_D.

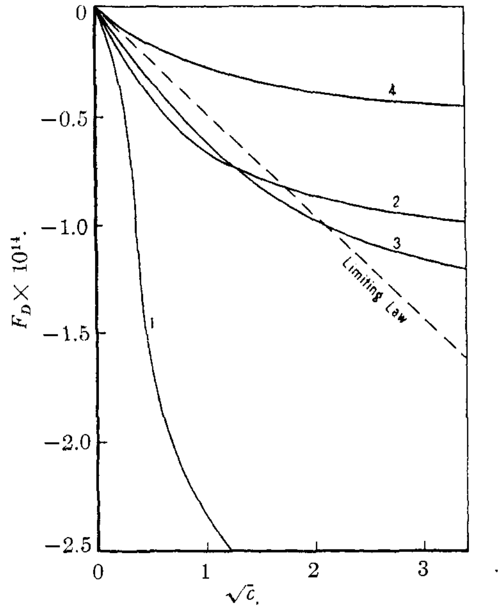

Fig. 3.—F_D as a function of c, F_D in ergs per ion × 10^{14}, c in moles/liter: Curve 1, $D_1 = 4$, $a = 3$, $R = 5$; curve 2, $D_1 = 25$, $a = 3$, $R = 10$; curve 3, $D_1 = 25$, $a = 2$, $R = 5$; curve 4, $D_1 = 49$, $a = 3$, $R = 5$.

Results of Calculation.—It is observed that the effect of a reduction in D near the central ion is to reduce a_{eff}, and to give lower (more negative) values for F_D. For values of D_1 down to the neighborhood of 25, a_{eff} remains positive for reasonable values of a and R, and in this region is in many cases approximately constant against changes in c. For values of D_1 below 25, however,

TABLE I

Assumed values	Quantity calculated	10	1.0	0.1	0.01	0.001	0.0001	0.00001
c moles/liter		10	1.0	0.1	0.01	0.001	0.0001	0.00001
Limiting law value ergs $\times 10^{16}$		1526	482.6	152.6	48.26	15.26	4.826	1.526
$D_1 = 4$	F_D	3486	2353.2	722.1	121.4	22.94	5.61	1.573
$a = 3$	Ratio	2.285	4.876	4.732	2.515	1.503	1.162	1.031
$R = 5$	a_{eff}	−0.541	−2.41	−7.59	−18.31	−32.2	−42.5	−28.7[a]
$D_1 = 4$	F_D	7525	5256.8[b]	1827.6	282.8	39.84	7.26	1.738
$a = 2$	Ratio	4.931	10.893	11.98	5.86	2.611	1.504	1.139
$R = 5$	a_{eff}	−0.767	−2.76	−8.81	−25.2	−59.3	−101.7	−117.3[a]
$D_1 = 4$	F_D		182.4	100.4	41.31	14.51	4.768	
$a = 5$	Ratio		0.378	0.658	0.856	0.951	0.986	
$R = 5$	a_{eff}		5.00	5.00	5.11	4.94	4.56[a]	
$D_1 = 25$	F_D	672.6	378.4[b]	142.16	47.10	15.139	4.818	
$a = 3$	Ratio	0.441	0.784	0.932	0.976	0.992	0.99835	
$R = 5$	a_{eff}	1.218	0.838	0.705	0.748	0.768	0.51	
$D_1 = 25$	F_D	1184.3	627.1[b]	193.39	53.39	15.81		
$a = 2$	Ratio	0.776	1.300	1.267	1.106	1.036		
$R = 5$	a_{eff}	0.277	−0.701	−2.03	−2.92	−3.32		
$D_1 = 25$	F_D[b]	986.7[b]	663.3[b]	259.4[b]	65.58	17.20	5.024	
$a = 3$	Ratio	0.647	1.374	1.700	1.359	1.127	1.041	
$R = 10$	a_{eff}	0.526	−0.829	−3.96	−8.04	−10.85	−11.98	
$D_1 = 49$	F_D	448.5	274.3	122.2	44.66	14.88	4.786	
$a = 3$	Ratio	0.294	0.568	0.801	0.925	0.975	0.9917	
$R = 5$	a_{eff}	2.31	2.31	2.39	2.44	2.47	2.54	
$D_1 = 49$	F_D	675.21	367.80	140.74	47.042	15.137		
$a = 2$	Ratio	0.443	0.762	0.922	0.975	0.9920		
$R = 5$	a_{eff}	1.21	0.950	0.810	0.788	0.780		
$D_1 = 49$	F_D	536.98	347.08[b]	147.15[b]	48.46	15.31[b]		
$a = 3$	Ratio	0.352	0.719	0.964	1.00415	1.0031		
$R = 10$	a_{eff}	1.77	1.196	0.356	−0.127	−0.296		
$D_1 = 75$	F_D	376.07	245.10	116.72	43.98	14.804		
$a = 3$	Ratio	0.246	0.487	0.765	0.911	0.970		
$R = 5$	a_{eff}	2.94	2.94	2.96	2.96	2.96		
$D_1 = 75$	F_D	388.54	255.89	122.56	45.678	15.072		
$a = 3$	Ratio	0.255	0.530	0.803	0.946	0.988		
$R = 50$	a_{eff}	2.81	2.69	2.36	1.72	1.20		
$D_1 = 100$	F_D	344.6	233.21	114.47	43.69	14.77		
$a = 3$	Ratio	0.226	0.483	0.750	0.905	0.968		
$R = 5$	a_{eff}	3.30	3.25	3.20	3.18	3.17		

[a] These values are probably too low. It would be very laborious to improve them, however, as they are based on F_D values which are very small differences between much larger numbers. [b] In these intervals additional F_D values were calculated for use in preparing the curves.

and even for $D_1 > 25$ if $R - a$ is large enough, a_{eff} is negative for high dilutions, and not at all constant. For these cases, and with a values approximating ordinary crystal radius sums, the ratio of F_D to the limiting law value is greater than unity, and the very high dilutions in which this ratio is still appreciably different from unity when $D_1 = 4$ are very striking. In the limit of high concentrations the ratio always becomes less than unity, and for the theoretical case of concentration approaching infinity it would go asymptotically to zero. This means that for $D_1 < 25$, say, the curve for F_D against $\sqrt{c}$ (which, as indicated above, can represent a curve of log $\gamma_{\pm}$ against $\sqrt{c}$) starts out with negative deviations from the straight line representing the limiting law, passes through an inflection, and finally crosses the limiting law line. Within a certain range of values of a, R and D_1, the negative deviations are not too large and the curve is nearly linear over a considerable concentration range in the neighborhood of the inflection. This produces the effect, also shown in curves obtained by Bjerrum[6] and by Gronwall,

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(6) N. Bjerrum, *Kgl. Dansk. Videnskab. Selskab. Math. fys. Medd.*, 7, 9 (1926).

LaMer and Sandved,[7] of a linear dependence on $\sqrt{c}$, with a slope greater than that of the limiting law.

The lowering of F_D produced by a reduction in D_1 can be interpreted on the basis of the molecular picture. The greater forces acting between ions in a medium of low dielectric constant will produce in Region I both a greater accumulation of oppositely charged ions than the simple Debye–Hückel theory provides, and an enhanced attraction exerted by each of these ions upon the central ion. There will thus be a double action tending to reduce the escaping tendency of the latter. When this escaping tendency is reduced below the limiting law value a_{eff} becomes negative. As will be discussed more fully below, the effect can be interpreted as an association, so that the similarity between some of our curves and those of Bjerrum and of Gronwall, LaMer and Sandved is more than an accident.

Probable Value of D_1.—Of the many publications in which the dielectric constant in electrolytic solutions has been discussed, the ones which will be most useful in helping us estimate the practical values which D_1 should assume are those of Debye,[8] Kossiakoff and Harker,[9] Schwarzenbach,[10] and Dunning and Shutt,[11] in which many references to other works are cited. Debye gives a theoretical curve, which we reproduce as the continuous curve of Fig. 4, for the effective radial dielectric constant as a function of distance from a central ion. Kossiakoff and Harker show that by using the Debye value $D_1 = 3$ to distances up to $r = 3$ Å. they can obtain very satisfactory calculations for the relative strengths of a larger number of inorganic oxygen acids. It also appears from their work that a value of D_1 appreciably different from 3.0 would destroy the agreement which they obtain. Schwarzenbach gives reasons for believing that the ratio of the acid strengths of the mono- and di-hydrochlorides in a series of polymethylene diamines is determined almost entirely by the mutual electrostatic potential energy of the two point charges. By making plausible assumptions regarding the configurations of the molecules he is thus able to give this energy numerically as a function of the distance separating the charges. His values permit the calculation of effective dielectric constants from the relation $\epsilon = e^2/rD_{\text{eff}}$. Values of D_{eff} so computed are shown as dots in Fig. 4. It is seen that they are in good qualitative agreement with the Debye curve. Finally, Dunning and Shutt show by means of accurate measurements of the macroscopic dielectric constant in a number of electrolyte solutions that the "saturation effect" due to the lowering of local dielectric constant about the ions can be satisfactorily represented by a numerical coefficient of the same order of magnitude as that calculated by Sack[12] on the basis of the Debye theory.

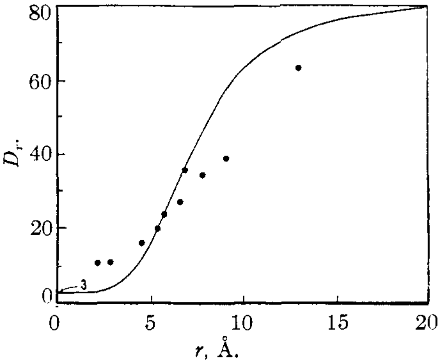

Fig. 4.—Local radial dielectric constant as a function of distance from a point charge in water: solid curve, Debye theory; points, values derived from Schwarzenbach's data (see text).

The Debye theory, and the Sack relation which is derived from it for the macroscopic dielectric constant of a salt solution, are based on the Mosotti hypothesis which Onsager[13] has shown to be inapplicable in aqueous media. There seems, on the other hand, to be no such difficulty in principle in accepting the results of Kossiakoff and Harker. From these, therefore, we should be able to conclude that in the near neighborhood of a central ion the value of D is equal to 3.0. However, for the purposes of the Debye–Pauling theory we are not interested in a region containing only one ion, but rather in the effective dielectric constant governing the electrostatic forces between two ions when they are rather close together. The Schwarzenbach case resembles this closely, but differs in that there the two charged centers have charges of the same sign, and are separated by a hydrocarbon chain in addition to the water molecules lying between them. The two ions in our

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(7) T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

(8) P. Debye, "Polare Molekeln," Leipzig, 1929, p. 133.

(9) A. Kossiakoff and D. Harker, THIS JOURNAL, **60**, 2047 (1938).

(10) G. Schwarzenbach, *Z. physik. Chem.*, **A176**, 133 (1936).

(11) W. J. Dunning and W. J. Shutt, *Trans. Faraday Soc.*, **34**, 467 (1938).

(12) See Debye, "Polare Molekeln," p. 137.

(13) L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

case will partially neutralize each other's fields at some points, reinforcing them at others, and may also, perhaps, interact in some complicated way with the water structure. Our conclusions regarding the proper D_1 to use must therefore be rather qualitative in character, but we can hardly be far wrong if we take a value of about 10.

Application of the Debye–Pauling Theory.—Accepting the conclusion that D_1 out to a distance of 5 Å. most probably lies in the neighborhood of 10, that is, between the values 4 and 25 for which calculations of F_D have been made, we are led to an interesting result. Taking for a values ion-radius sums, using the crystal radii given by Pauling,[14] we must obtain as a general rule, even in very dilute solutions, appreciable negative deviations from the Debye–Hückel limiting law for activity coefficients. Since it is well known that such negative deviations are not the general rule, it is clear that the representation is at fault, and it becomes necessary to inquire into the sort of shortcoming which can be responsible for this difficulty.

In the first place, to superpose a Bjerrum[6] association correction on our treatment, or, what is generally assumed[15] to be roughly equivalent, to include the "higher terms" of Gronwall, LaMer and Sandved[7] in the Poisson–Boltzmann equation that is the basis of the theory, does not offer a way out. The Bjerrum critical radius within which ions are taken as being associated with the central ion is given as $r_c = z^2e^2/2DKT$ and, with D_1 ten times smaller than D_2, would be ten times larger than the customary 3.5 Å. for univalent ions. We would therefore have to take it equal to R, which it could not exceed. Due to this large value, and still more to the strong forces acting in Region I, the concentration of associated pairs would be so large as to produce negative deviations from the limiting law which would again be entirely outside the range of ordinary experience. Similar remarks can be made regarding the accumulation of oppositely charged ions in Region I given by the Gronwall–LaMer–Sandved theory. As will be seen below, the Debye–Pauling theory gives a concentration of oppositely charged ions in Region I which is too high. Neither the Bjerrum nor the Gronwall–LaMer–Sandved considerations relieve this difficulty.

Change in the macroscopic dielectric constant is likewise unable to help. For Dunning and Shutt[11] have confirmed experimentally the theoretical predictions of Debye and Falkenhagen[16] of an initial increase in D when small amounts of electrolytes are added to water, whereas Hückel,[17] in order to get a raising of log γ similar to what we want here, had to assume a decrease in D with increasing concentration.

A number of other effects[18] have been considered from time to time in discussing the individualities of activity coefficients, but none of these is calculated to account for such large deviations in such dilute solutions as the ones in question here.

The Association–Hydration Model.—Inspection of Table I shows that without discarding the Debye–Pauling representation the large deviations from the limiting law referred to above can be avoided by taking a equal to or only slightly less than R. This suggests a picture of ionic solutions which has some very attractive features. The water layer immediately surrounding an ion is held to it by forces which have been discussed by numerous workers.[19] If these forces are so strong that the layers are never penetrated when the ions approach each other, and if we assume that it is only within such a layer that dielectric saturation occurs, then we must clearly write $a = R$, assigning a numerical value equal to the conventional radius sum plus two water layers each, say, one molecule thick. The assumption that water more than one molecule distant from an ion is "normal" has been made before,[19] and we may tentatively accept it. In that case, for an alkali halide, for example, $a = R = 7$ or 8 Å. would be of something like the right order of magnitude. Permanent hydration of the sort described would raise the activity coefficient by the removal of water from its solvent function.[20] This, with the large Debye–Hückel a would give values to log $\gamma_\pm$ considerably higher than the experimental ones the alkali halides are known to have in dilute solution.

If, now, the water layers around the ions are not impenetrable, a close encounter of oppositely charged ions, accompanied by the breaking of

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(14) L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Ithaca, N. Y., 1940.

(15) *E. g.*, E. Güntelberg, "Studier over Elektrolyt-Aktiviteter," Copenhagen, 1938, p. 26, or R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge, 1940, p. 407.

(16) P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 121 (1928).

(17) E. Hückel, *ibid.*, **26**, 93 (1925).

(18) See, for example, G. Scatchard, *Chem. Rev.*, **19**, 309 (1936).

(19) (a) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933). (b) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

(20) N. Bjerrum, *Med. Vetenskapsak. Nobelinst.*, **5**, no. 16 (1919). Quoted by E. Güntelberg, ref. 15, p. 32.

these layers, may be assumed to be not only possible but also a reasonably probable occurrence. We may consider pairs to which this has happened as associated and, temporarily, out of action as members of the ionic population. For reasons discussed below this need not seem an arbitrary assumption. When two hydrated ions of opposite sign approach each other, then, we may imagine that they either separate again after coming no closer together than their intact hydration shells will allow, or else that they break each other's shells and become definitely associated. The proportion of encounters in which either of these events occurs will be a specific property of the kinds of ions involved. (The case of only one of the hydration envelopes being broken, so that the two ions are separated by a single water molecule, is discussed below. For the time being we ignore it.)

This sort of behavior can be treated in either of two ways. On the Debye–Pauling representation we would have R = 7 Å., say, and a somewhat less as a statistical average of the case where the ions remained separate, $a = 7$, and the case where they went together, $a = 3$, say. The average value may be obtained by preparing a weighted average of the corresponding values of F_D and finding what assumed a value would give the same figure. Calculations for R = 7 Å. and $D_1 = 4$ show, for example, that the same F_D is obtained by taking a = 6.4 Å. as by assuming that $a = 3$ one per cent. of the time and $a = 7$ ninety-nine per cent. of the time, very nearly the same percentages being obtained at assumed concentrations of 0.01 and 0.001 mole/liter. The values of a_{eff} obtained for these two concentrations are 4.6 and 4.8 Å., respectively, well within the range of values given by experiment. A "degree of association" for each case can be computed by integrating the electric density in Region I for a = 3 Å., the result being a total charge in this region of $-0.1086\ ze$ when $c = 0.01$ and $-0.0119\ ze$ when $c = 0.001$. If this is interpreted as the fraction of the time a whole ion (of charge equal and opposite to that of the central ion) spends in Region I for a = 3 Å. we get a degree of association of about 0.001 for $c = 0.01$ and of about 0.0001 for $c = 0.001$. These values are in qualitative agreement with the requirements of the mass-action law.

The other treatment would ignore the associated pairs except for taking cognizance of the fact that they had disappeared from the ionic population, and for the assumption that their formation is a chemical process and their equilibrium concentration calculable from an equilibrium constant. This point of view regards the solute as hydrated and partially associated. Using the Debye–Hückel first approximation with a = 7 Å., and assuming that each ion binds q water molecules and that K is the *association* constant of the pairs, we can combine terms originating with Bjerrum[20] and with the classical Arrhenius theory and obtain an approximate expression for log $\gamma_\pm$ for a uni-univalent salt

$$\log \gamma_\pm = \frac{-0.59\sqrt{c}}{1 + 0.329 \times 7 \times \sqrt{c}} + \left[\frac{2(q_+ + v_-)}{2.303 \times 55.51} - \frac{K}{2.303}\right] m$$

This equation will be accurate only for very dilute solutions, as both the terms in the coefficient of m are subject to activity corrections. The use of the Debye–Hückel first approximation would seem, however, to be very well justified by the large values that a will always have on this representation. This equation is very similar to one given by Guggenheim,[21] and to the empirical ones used, for example, by MacInnes[22] and his co-workers. Comparing with Guggenheim's equation and taking the numerical values he gives for the coefficient of the linear term, and assuming that $q_+ = q_- = 4$, we find that K must be of order of magnitude unity to satisfy the experimental data for alkali halides in the dilute range. This corresponds to a degree of association of 1% at $c = 0.01$.

The degrees of association calculated by the different methods of the last two paragraphs cannot be expected to agree for the sort of choice of constants that was made. Qualitatively, however, the results are what we would look for. By using the Debye–Pauling formulation with $D_1 = 4$, that is, too small a value, we give to each ion in Region I too large an effect. Rough agreement with experimental activity coefficients is therefore obtained with a degree of association much less than the more realistic "chemical" method needs to produce a similar effect. We could repeat the calculations using $D_1 = 9$, say, but this would hardly repay the effort as there are other restrictions on the quantitative applicability of the Debye–Pauling picture. For example, although

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(21) E. A. Guggenheim, *Phil. Mag.*, [7] **19**, 588 (1935); **22**, 322 (1936).

(22) A. S. Brown and D. A. MacInnes, THIS JOURNAL, **57**, 1356 (1935); T. Shedlovsky and D. A. MacInnes, *ibid.*, **58**, 1970 (1936).

the central ion is provided with its own region of special dielectric constant, the cloud ions are still pictured as being immersed in a medium of uniform D. What is worse, we are going to see that the distribution of cloud ions near the central ion is not dominated by electrostatic forces, but by the structure of the liquid. This means that the Poisson–Boltzmann equation will lose its validity there. While this does not throw out the qualitative or semi-quantitative representation, it discourages attempts at fully quantitative comparison with the results of other treatments.

Further Analysis of the Model.—The acceptability of the hydration–association picture must depend chiefly upon the answers to two questions. One is whether the definition of association it uses is sufficiently free from arbitrariness. In the light of modern ideas of the structure of liquids this can almost certainly be answered in the affirmative. The natural criterion of definiteness of association, and that used by Bjerrum[6] and Fuoss,[23] is that there shall be no large number of ion pairs in states intermediate between those definitely associated or dissociated. Bjerrum and Fuoss found that the distribution function derived from electrostatic forces in a uniform dielectric medium was able to satisfy this criterion. It seems, however, that the criterion is even better satisfied by the structure of the liquid. X-Ray studies of liquid systems,[24] including water[25] and ionic solutions,[26] give a distribution function which makes a definite distinction between nearest neighbor molecules and next nearest neighbors. Successful theories of viscosity,[27] conductance[28] and diffusion[29] have been based on the idea that when a molecule or ion moves from one "mean location" to another it does so by a kind of jump, spending proportionately very little time in intermediate positions. It therefore seems justifiable to conclude that association of ions in the sense in which we have used it here is a sufficiently clear-cut concept. The addition of a third solute species—an ion pair with one water molecule between the ions—is required, as mentioned above, to make the representation formally complete. A pair of this sort could, according to choice, be treated conventionally either as associated or as non-associated. In the first case two associated species with different K values would have to be taken into account. In the second the ions would contribute to the ionic strength and an appropriate average a would have to be used.

The other question is whether the dissociation constants of order of magnitude unity required by the theory are in reasonable agreement with what other considerations would lead us to expect. K of order unity means ΔF^0 for association about zero, and we have therefore to see whether ΔF^0, estimated from the molecular picture, can be expected to have a zero value. We shall assume that the main process is the removal of one water molecule from each of the ions involved, and the subsequent formation of the corresponding ion–ion pair and of the water–water pair. In this process the other water molecules attached to the ions and to the "reacting" water molecules will change in position and in tightness of attachment, but if we make electrostatic calculations using a dielectric constant the latter is designed to take care of these changes as well as of readjustments made by more distant parts of the medium. The choice of the value to use for the dielectric constant is rather arbitrary in the case of the ion–ion interaction. Our choice of 9 has some support from our earlier discussion of the probable value of D_I, but is also somewhat *ad hoc*. For the ion–dipole interaction, $D = 3$ following Kossiakoff and Harker[9] seems a less arbitrary choice. For the dipole–dipole interaction of the water molecules we again use $D = 3$, since the water structure can be expected to be rather definite around a water–water pair, and can therefore be imagined not to "give" much as the pair is formed. This is quite arbitrary, but as this term does not dominate the result, and in any case has no influence on the relative values of ΔF^0 for different salts, the specific assumption is less important. Considering sodium chloride, then, and taking[14] $r_+ = 0.96$ Å., $r = 1.81$ Å., $\mu_{H_2O} = 1.85 \times 10^{-18}$, r_{H_2O} toward a positive ion $= 1.03$ Å., r_{H_2O} toward a negative ion $= 1.73$ Å.,[30] and $d_{H_2O-H_2O} = 2.76$ Å. we compute the various electrostatic energies. The van der Waals attractive energies are computed from values of the ionization potential I

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(23) R. M. Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).

(24) *E. g.*, G. W. Stewart, *Chem. Rev.*, **6**, 483 (1929); H. Menke, *Physik. Z.*, **33**, 593 (1932).

(25) J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

(26) G. W. Stewart, *ibid.*, **7**, 869 (1939).

(27) H. Eyring, *ibid.*, **4**, 283 (1936).

(28) M. Polissar, *ibid.*, **6**, 833 (1938).

(29) A. E. Stearn, E. M. Irish, and H. Eyring, *J. Phys. Chem.*, **44**, 981 (1940).

(30) These water radii were obtained by averaging the covalent and van der Waals radii for H and O given by Pauling.[14] This was done because the "hydrogen bond distance" in ice (O–O = 2.76 minus O–H = 0.97, or 1.79) is given very closely by the sum of these average radii ($^1/_2(1.4 + 0.66) + {}^1/_2(1.2 + 0.31) = 1.79$).

and the polarizability α used by Bernal and Fowler[19] for water, and by Mayer[31] for the ions. The repulsive energies are computed from the expression $E_r = Be^{-r/\rho}$, using Mayer's[31] value 0.345×10^{-8} for ρ and determining B from the values of the equilibrium separations given by the radius sums. The net result for the energy increment on association for sodium chloride is -3.08 kcal./mole.

This is a free energy increment ΔF, since the dielectric constant is supposed to account for the entropy changes in the medium. ΔF^0 can therefore be obtained by subtracting $T\Delta S^0$, this ΔS^0 being the gain in entropy when two ions (calculated as gas molecules at a concentration of 1 mole/liter) unite. ΔS^0 for this case comes out -11.3 E. U., providing at 300°K. a contribution to ΔF^0 of about $+3.39$ kcal./mole. This approximately balances off the energy contributions and gives the result $\Delta F^0 = +0.31 (\simeq$ zero, since the rational unit for ΔF^0 is 1.365 kcal./mole the quantity corresponding to a factor of 10 in K).

It is obvious that very different results could be obtained with different choices of constants (*e. g.*, $\Delta F^0 \simeq -22$ kcal./mole for $D = 3$ throughout) and also that considerable liberties have been taken with the methods of calculation. The use of a dielectric constant for so "coarse-grained" an effect, particularly for the purposes it is here called upon to serve, rather overloads the concept, and allowing it to change during the course of the association process is objectionable. More must also be said about the entropy change (see below). It is probably justifiable to conclude, however, that $K = 1$ is at any rate not more unreasonable than $K > 10$ or $K < 0.1$.

Discussion

The hydration–association model has been introduced here for the purpose of obtaining a physically reasonable interpretation of the arithmetical consequences of the Debye–Pauling equation. Beyond its ability to give this, however, the model has some other attractive features. One of these is that it gives a way of taking explicit account of the "short-range" forces that are known to be important in electrolyte behavior. Qualitatively, it interprets Guggenheim's[21] interaction coefficients (themselves introduced for the purpose of giving a quantitative form to Brönsted's[32] "Principle of Specific Interaction") in terms of dissociation constants and specific q's and a's. Whether or not the K's will be found to reflect small covalent contributions to some of the energies, there can be no doubt that K is specific for the particular kind of ion pair to which it refers. In fact, even in the crude form described above the calculation gives for the different alkali halides K values which show in a remarkable way the well-known trends in their activity coefficients. This is seen in Table II, where the calculated ΔF^0 of association is recorded for each of the twenty salts. A large number means a small tendency toward association, and therefore, at a given concentration, a high activity. It is seen that on this basis the table predicts $\gamma_{\mathrm{MI}} > \gamma_{\mathrm{MBr}} > \gamma_{\mathrm{MCl}} > \gamma_{\mathrm{MF}}$ for $\mathrm{M}^+ =$ any alkali ion, whereas $\gamma_{\mathrm{LiX}} > \gamma_{\mathrm{NaX}} > \gamma_{\mathrm{KX}} > \gamma_{\mathrm{RbX}} > \gamma_{\mathrm{CsX}}$, $\mathrm{X}^- =$ any halide ion except F^-. For the fluorides the table shows definite signs of the inversion in order, compared with the other halides, which is actually found in the activity coefficients. The inversion in order found experimentally for the cesium salts does not appear in the table, though a trend in that direction with larger M^+ is discernible. The values for the rubidium and cesium compounds have a tendency to fall out of line when the various alkali salts of one halogen are compared. It is possible that this disturbance could be removed by adjustment of some of the constants in the energy calculations. No attempt has been made to do this, however, partly because it is quite possible that other specific structural effects are involved, and partly because one of the most striking things about the table is the fact that the results in it were obtained with constants which had been chosen for a different purpose, namely, to make ΔF^0 approximately equal to zero for sodium chloride only. It may be added that taking account of the effect of ionic sizes in the Debye–Hückel term in log $\gamma_\pm$ by writing $a = r_+ + r_- + 5$ Å. does not alter any of these relationships.

TABLE II

ΔF^0 OF ASSOCIATION IN KILOGRAM CALORIES PER MOLE

	Li	Na	K	Rb	Cs
F	−0.63	−0.68	−0.74	−0.63	−0.52
Cl	+1.24	+ .31	− .24	− .07	− .08
Br	+1.25	+ .61	+ .21	+ .26	+ .13
I	+1.77	+1.00	+ .46	+ .43	+ .45

It should be mentioned that the van der Waals attractive energies as here calculated are cer-

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(31) J. E. Mayer, *J. Chem. Phys.*, **1**, 270 (1933).

(32) J. N. Brönsted, THIS JOURNAL, **44**, 877 (1922).

tainly wrong, partly because the equation employed is a rough one

$$E = -{}^3/_2 \frac{I_1I_2\alpha_1\alpha_2}{(I_1 + I_2)r^6}$$

and partly also because each ion was taken as having a constant ionization potential and polarizability throughout, whereas Mayer[31] has shown that the effective values of these "constants" vary from compound to compound. Taking Mayer's attractive coefficients for the various alkali halide pairs would probably not be an improvement, however, as corresponding values are not available for the ion-water pairs with which comparison must be made. As a matter of fact, the influence of these van der Waals contributions is very minor, and the table would be altered only trivially if they were omitted.

The entropy terms for association are also doubtless wrong, for with such a structure as we know the solution to possess it is rather absurd to write the rotational partition function of the ion pair as if the latter were a diatomic gas molecule. The serial order and separation of the values for the different halides of the same alkali metal or for the different alkali salts of the same halogen may well be given correctly by such a calculation, however. It is in the entropy terms also that specific structural effects might be expected to show up if such exist. This might mean that if we desired to keep the present form of calculation specific differences would have to appear in the dielectric constant values used.

One is tempted to imagine that the agreements between the trends shown in Table II and the known trends in activity coefficients are not entirely fortuitous. If there is anything real in them, they may be taken as lending some *a posteriori* support to the energy calculations, which might then be more reliable than the assumptions entering into them would justify us in expecting. Further light on this question can doubtless be obtained from a more extended study of the exact values and the constancy of the K's obtained from activity data. Such a study can presumably also throw light on the question of the semi-associated pairs that have been mentioned above, though we are probably justified, as a "zero'th approximation," in omitting to take them further into account here. It appears at first sight that their concentration should be small compared either with the fully associated or fully dissociated pairs. The net process in their formation is the breaking of one water bond and the formation of another. The latter is presumably somewhat more stable than the former, but this should hardly be enough to make the process comparable in importance to the formation of a fully associated pair.

Another important consequence of the hydration of the ions should be mentioned. Without having been assumed for this purpose, it will nevertheless produce the effect of raising the stoichiometric activity coefficient above unity in concentrated solutions of slightly associated salts. This is again in agreement with experience. Salts made up of ions with no large tendency to hydrate, nitrates, for example, will not be expected to show this effect. It must be pointed out in this connection that in the hydration-association picture, since all configurations in which the hydration shells are broken are considered as examples of association, the hydration layer must in every case be considered as a part of the dissociated ion. If this layer is not very tight, as in the case of nitrate ion, this will manifest itself in a correspondingly great formal "tendency to associate." The hydration "correction" to the expression for log $\gamma_\pm$ must therefore always be made, and a value for a must always be used which includes the thickness of two hydration layers. This is a very great advantage, for with such large values of a the Debye-Hückel first approximation can be expected to be quite accurate, and the influence of local dielectric constant can presumably be omitted from the ion-cloud effect entirely.

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Summary

1. A new derivation is given for the Debye-Pauling expression for the effect of local dielectric constant on the electrostatic free energy of a central ion due to its ion cloud.

2. It is shown that if the local dielectric constant is less than 25, and if the ions can approach each other to distances equal to their crystal radius sums, the complete Debye-Pauling expression predicts large negative deviations from the Debye-Hückel limiting law for activity coefficients even in very dilute solution. This prediction is in disagreement with experiment.

3. It is shown that agreement between experimental activity coefficients and the predictions of the Debye–Pauling theory can be obtained by assuming that the ions in aqueous solution are hydrated and that they take part in an association equilibrium. The existence of such an equilibrium is shown to be in harmony with modern views of the structure of liquids.

4. Rough calculation yields values of the proper order of magnitude for the dissociation constants of the alkali halides. The relative values obtained for the different salts in this group are found to show some of the characteristic features observed in comparing their experimental activity coefficients.

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Polymolecular Solvolysis: Catalysis of the Racemization and the Hydrolysis of Optically Active α-Phenylethyl Halides by Polyhalide Metallic Salts

BY NICHOLAS T. FARINACCI

In previous studies,[1] the first order reactions of solvolysis were investigated to determine the type of mechanism involved in the alcoholysis of benzhydryl chloride and in the acetolysis of α-phenylethyl chloride. The optically active forms of the latter undergo reactions in hydroxylic solvents, such as water, the alcohols, acetic acid, etc., that yield products which are considerably racemized. A list of studies is included in Table I, for which both first and second order kinetics were observed.

TABLE I

HYDROLYSIS, ALCOHOLYSIS, ACETOLYSIS AND RACEMIZATION OF OPTICALLY ACTIVE α-PHENYLETHYL HALIDES IN VARIOUS SOLVENT MIXTURES

Ref.	Halide	Reaction medium	Temp., °C.
2	*d*-α-PhCHClMe	80% EtOH-H_2O	28.7
3	*d*-α-PhCHClMe	100% EtOH-$HgCl_2$	25
4	*l*-α-PhCHClMe	H_2O (two phases)	20
4	*l*-α-PhCHClMe	H_2O-KOH	20
4	*l*-α-PhCHClMe	60% Me_2CO-H_2O	70
4	*l*-α-PhCHClMe	80% Me_2CO-H_2O	70
4	*d*-α-PhCHClMe	100% MeOH	70
4	*d*-α-PhCHClMe	3.5 m. NaOMe in MeOH	70
4	*l*-α-PhCHClMe	100% EtOH	70
4	*l*-α-PhCHClMe	2.85 m. NaOEt in EtOH	70
4	*l*-α-PhCHClMe	H_2O	20
1b	*d*-α-PhCHClMe	100% HOAc	50
1b	*d*-α-PhCHClMe	100% Me_2CO, $N(Et)_4$-OAc	50
5	*l*-α-PhCHClMe	90 and 95% Me_2CO with	
5	*l*-α-PhCHClMe	$HgCl_2$ at various concns.	50
5	*l*-α-PhCHClMe	100% Me_2CO with $HgCl_2$	20
6	*l*-α-PhCHClMe	SO_2 with $N(Et)_4Cl$	..
7	*l*-α-PhCHBrMe	100% Me_2CO and Br^-	..

The generalization[8] that a second order displacement on an asymmetric carbon atom, the rate of which is proportional to the concentration of attacking ion, inverts the configuration is based on numerous studies. The validity of this principle was confirmed by experiments in which radioactive isotopes were used to follow the course of the substitution. When tagged iodide ions reacted with optically active halides, such as alkyl iodides, the specific rates were practically identical with the specific rates of racemization. This is required if every substitution on the asymmetric carbon atom inverts the configuration. Thus, the second-order reaction substantiated the stereo-

$$RI + I^{-*} \rightleftharpoons RI^* + I^-$$

chemical corollary of the London-Polanyi-Olson theory of substitution reactions that inversion was a part of the process. The R denotes the alkyl residue and the star refers to the radioactive isotope.[9]

The fact that a similar generalization could not be applied to the first-order substitution reactions of optically active halides offered a very interesting problem. One of the most logical explanations was that solvolytic reactions of this type involve carbonium ions which have a planar configuration and therefore result in racemized products.

The present study starts with the assumption that every substitution on an asymmetric carbon

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(1) (a) Farinacci and Hammett, THIS JOURNAL, **59**, 2542 (1937); (b) Steigman and Hammett, *ibid.*, **59**, 2536 (1937).

(2) Ward, *J. Chem. Soc.*, 445 (1927).

(3) Bodendorf and Boehme, *Ann.*, **516**, 1 (1935).

(4) Hughes, Ingold and Scott, *J. Chem. Soc.*, 1201 (1937).

(5) Read and Taylor, *ibid.*, 679 (1940).

(6) Bergmann and Polanyi, *Naturwissenschaften*, **21**, 378 (1933).

(7) Polanyi, Bergmann and Szabo, *Trans. Faraday Soc.*, **32**, 843 (1936).

(8) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); Olson, *J. Chem. Phys.*, **1**, 418 (1933).

(9) Hughes, Juliusburger, Masterman, Topley and Weiss, *J. Chem. Soc.*, 1525 (1935); Hughes, Juliusburger, Scott, Topley and Weiss, *ibid.*, 1173 (1936); Cowdrey, Hughes, Nevell and Wilson, *ibid.*, 209 (1938).