V_{12}, we obtain for φ_2 a value of 5.43 volts. This value for the work function of a WI surface is in satisfactory agreement with the value 5.27 volts calculated from surface ionization measurements by Hendricks, Phipps and Copley,[4] since their result was obtained by extrapolating data taken over a short temperature range.

The large negative value of the W–WI contact potential suggests that the adsorbed iodine atoms on the surface are highly polarized. Thus on the surface of the coated filament there is an electrical double layer with the negative ends of the dipoles facing out. The dipole moment μ of the adsorbed atoms may be estimated by the formula

$$\mu = V_{12}/2\pi \, \sigma \qquad (2)$$

where V_{12} is the contact potential and σ is the concentration of atoms per cm.[2]. Assuming that the measurements have been made on a complete monolayer and that the lattice structure is the same as for a cesium film,[11] σ may be taken as 4.8 $\times$ 10[14] atoms cm.[-2]. Substituting in equation (2) gives a value of 1.0 Debye units for μ.

Summary

Evidence is presented that iodine forms a stable film on tungsten. Above 1250°K. the film evaporates at a noticeable rate, but flashing to 2000°K. is required for its complete and rapid removal.

The contact potential difference at room temperature between a clean tungsten surface and an iodine-coated tungsten surface was found to be −0.91 volt. The magnitude of the dipole moment of the adsorbed atoms in the complete film is estimated as 1.0 Debye unit.

(11) Taylor and Langmuir, *Phys. Rev.*, **44**, 423 (1933).

Activity Coefficients in Concentrated Aqueous Solutions of Strong Electrolytes Described by a Formula Containing the Mean Ionic Diameter as Single Parameter. I. Theory and Application to the Alkali Chlorides, Bromides and Iodides[1]

BY PIERRE VAN RYSSELBERGHE AND SYLVAN EISENBERG

I. Introduction

If one wishes to represent the activity coefficient of a strong electrolyte by means of a formula valid at all concentrations, from infinite dilution to saturation, it is usually assumed necessary to introduce two parameters: the mean ionic diameter or distance of closest approach between a positive and a negative ion, a, and a coefficient B which, multiplied by the first power of the concentration C, gives a term representing, in a purely empirical manner, the effect of repulsive forces. The corresponding formula is associated with the names of Hückel[2a] and Harned,[2b] and can be written as follows, in the case of one single electrolyte being present

$$\log f_{\pm} = -\frac{z_+ z_- \epsilon^2 \kappa}{2DkT(1 + \kappa a)} + BC \qquad (1)$$

in which $f_{\pm}$ is the mean rational activity coefficient of the ions, z_+ and z_- are the absolute values

(1) Paper presented at the Meeting of the Pacific Division, American Association for the Advancement of Science, Stanford University, June, 1939.

(2) (a) E. Hückel, *Physik. Z.*, **26**, 93 (1925); (b) H. S. Harned, Chap. XII of Taylor's "Treatise on Physical Chemistry," 2d ed., pp. 797, *et seq.*, D. Van Nostrand and Co., New York, 1931, where earlier references will be found.

of the valences of the positive and of the negative ions, ϵ is the elementary charge of positive electricity, D is the dielectric constant of the solvent, k is Boltzmann's constant, T is the absolute temperature, κ is defined by the formula

$$\kappa = \sqrt{\frac{4\pi n \epsilon^2 (\nu_+ \nu_+^2 + \nu_- z_-^2)}{DkT}} \qquad (2)$$

in which n is the number of molecules of salt per cc., ν_+ and ν_- the numbers of positive and negative ions corresponding to one molecule of salt. The reciprocal of κ is often designated as the *radius of the ionic atmosphere*. The number n and the concentration C are connected by the formula

$$C = n \times 1000/N \qquad (3)$$

in which N is Avogadro's number.

For aqueous solutions of uni-univalent electrolytes at 25°, formula (1) can be transformed into the following

$$\log_{10} f_{\pm} = -0.5059 \frac{\sqrt{C}}{1 + \frac{a}{3.042}\sqrt{C}} + BC \qquad (4)$$

in which a is expressed in Ångströms.[3]

(3) The numerical values of the constants used are: $\epsilon = 4.770 \times 10^{-10}$, $\pi = 3.1416$, $N = 6.064 \times 10^{23}$, $D = 78.54$, $k = 1.371 \times 10^{-16}$, $T = 298.1$, log 10 = 2.3026.

The first term on the right of formula (1) or (4) represents the decrease in thermodynamic activity due to the electrostatic interactions between ions, while the second term, in which the empirical constant B is positive, represents the combined effect of short-range repulsive forces between ions, interaction between ions and solvent, possible departure from complete dissociation at high concentrations, variation of dielectric constant with concentration, deviations from spherical symmetry for the ions, etc. The first term results from the Debye–Hückel theory; the second one corresponds, at least in some respects, to the van der Waals forces between molecules of gases or liquids. Therefore, we shall designate these terms as Debye–Hückel (D. H.) and van der Waals (W.) terms, respectively. When the W. term becomes larger than the D. H. term as concentration rises, the repulsive forces outweigh the electrostatic attractions between ions and their atmospheres, and the activity coefficient becomes larger than unity. In an interesting discussion of the properties of concentrated electrolytes, Onsager[4] suggests expressing the W. term as an ordinary covolume correction of van der Waals, which amounts to considering the repulsive forces as having a potential equal to zero at all distances r larger than a from the center of each ion and rising suddenly to infinity at $r = a$. Onsager states that the values of a to be introduced in the W. term "need not agree exactly with those that are used in computing the coulomb energy, because the picture of 'hard billiard balls' is certainly too simple." He states, however, that "there seems to be a fairly close correspondence. A more complete study of this question might be worth while; it would show to what extent the thermodynamic functions of different electrolytes form a one-parameter family in regard to their dependence on the concentration, and give us more detailed information about the short-range forces." The present work is an answer to this query. The first step is to establish as correct an expression as possible for the W. term, taking into account excluded spheres, overlapping of such spheres, etc. Both the D. H. and the new W. terms are then expressed in terms of the same a and the activity coefficient is represented by a *one-parameter* formula. The theory leading to the new expression for the W. term is given in the next section. The resulting formula is then ap-

plied to a systematic interpretation of the activity data of the alkali chlorides, bromides and iodides. Other salts will be studied in subsequent communications.

We should note here that a remarkable attempt at setting up a one-parameter formula is Guggenheim's[5] modification of Brönsted's specific interaction theory, in which the D. H. term contains the same a (3.08 Å. at 0°) for all electrolytes, and the W. term is linear in the concentration, the coefficient being the parameter and representing the specific interaction between positive and negative ions. This formulation is satisfactory at ionic strengths lower than 0.1 and the parameter has the interesting property of conserving its value in all mixtures where the corresponding pair of ions is present.

II.   The van der Waals or Covolume Terms in the Activity Coefficient of a Strong Electrolyte

The problem before us is to compute the partition function representing the mutual exclusion from certain portions of space of a mixture of N_α molecules of one kind and N_β molecules of another kind. The diameters of these ions are, respectively, D_α and D_β. The problem is extremely complicated and, as noted by Fowler,[6] several solutions to be found in the literature are entirely fallacious. In the second edition of his "Statistical Mechanics," Fowler gives a solution due to Ursell,[7] which supersedes all previous ones. Ursell's theory is quite general and can be applied to a mixture of any number of kinds of molecules. He treats completely the case of two kinds and finds for the partition function [$B(T)$ in Ursell's notation]

$$Z = V^{N_\alpha + N_\beta} Y \tag{5}$$

with

$$\log Y = -\frac{1}{V}\left\{ N_\alpha^2\left(\frac{2}{3}\pi D_\alpha^3\right) + N_\alpha N_\beta\left(\frac{4}{3}\pi D_{\alpha\beta}^3\right) + N_\beta^2\left(\frac{2}{3}\pi D_\beta^3\right)\right\} - \frac{1}{V^2}\left[\frac{5}{16}N_\alpha^3\left(\frac{2}{3}\pi D_\alpha^3\right)^2 + 4\pi^2 N_\alpha^2 N_\beta D_\alpha^3\left\{\frac{2}{9}D_{\alpha\beta}^3 - \frac{1}{8}D_{\alpha\beta}^2 D_\alpha + \frac{1}{144}D_\alpha^3\right\} + \frac{5}{16}N_\beta^3\left(\frac{2}{3}\pi D_\beta^3\right)^2 + 4\pi^2 N_\alpha N_\beta^2 D_\beta^3\left\{\frac{2}{9}D_{\alpha\beta}^3 - \frac{1}{8}D_{\alpha\beta}^2 D_\beta + \frac{1}{144}D_\beta^3\right\}\right] \tag{6}$$

In this formula $D_{\alpha\beta}$ is the sum of the radii of the two kinds of molecules. We thus have

$$D_{\alpha\beta} = (D_\alpha + D_\beta)/2 \tag{7}$$

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(4) L. Onsager, *Chem. Rev.*, **13**, 73 (1933).

(5) E. A. Guggenheim, *Phil. Mag.*, [7] **19**, 588 (1935).

(6) R. H. Fowler, "Statistical Mechanics," 2nd edition, Cambridge University Press, 1936, pp. 241 *et seq.*

(7) H. D. Ursell, *Proc. Camb. Phil. Soc.*, **23**, 685 (1927).

In applying this result to electrolytes we shall assume that

$$D_\alpha = D_\beta = D_{\alpha\beta} = a \qquad (8)$$

a being the distance of closest approach which also appears in the D. H. term. If N is the number of molecules of salt in the volume V we have

$$N_\alpha = \nu_+ N \qquad N_\beta = \nu_- N \qquad (9)$$

Taking (8) and (9) into account, formula (6) becomes

$$\log Y = -\frac{N^2}{V}(\nu_+ + \nu_-)^2 \left(\frac{2}{3}\pi a^3\right) - \frac{5}{16}\frac{N^3}{V^2}(\nu_+ + \nu_-)^3 \left(\frac{2}{3}\pi a^3\right)^2 \quad (10)$$

Let

$$v = \frac{4}{3}\pi a^3 \qquad (11)$$

represent the volume of the sphere of protection of an ion. Formula (10) becomes, making $\nu_+ + \nu_- = \nu$

$$\log Y = -\frac{\nu^2 N^2}{2V}v - \frac{5\nu^3 N^3}{64 V^2}v^2 \qquad (12)$$

or, expressing it in terms of the total number of ions present, $N_i = N_\alpha + N_\beta = \nu N$

$$\log Y = -\frac{1}{2}\frac{N_i^2}{V}v - \frac{5}{64}\frac{N_i^3}{V^2}v^2 \qquad (13)$$

The corresponding contribution to the Helmholtz free energy of the ions in the solution is

$$F_{iw} = -kT \log Y = N_i kT \left[\frac{1}{2}\frac{N_i}{V}v + \frac{5}{64}\left(\frac{N_i}{V}\right)^2 v^2\right] \quad (14)$$

On account of the practical incompressibility of solutions, F_{iw} can be assumed equal to the corresponding Gibbs free energy G_{iw} which is such that

$$G_{iw} = N_i \Delta\mu_{iw} = N_i kT \log f_{\pm w} \qquad (15)$$

in which $\log f_{\pm w}$ corresponds to the van der Waals term in $\log f_\pm$. From (14) and (15) we deduce

$$\log f_\pm = \frac{1}{2}\frac{N_i}{V}v + \frac{5}{64}\left(\frac{N_i}{V}\right)^2 v^2 \qquad (16)$$

or, in terms of the molar concentration C and Avogadro's number N

$$\log f_\pm = \frac{1}{2}v\nu NC \times 10^{-3} + \frac{5}{64}v^2\nu^2 N^2 C^2 \times 10^{-6} \quad (17)$$

Expressing a in Ångström units we have, when $\nu = 2$

$$\log_{10} f_\pm = 1.10313 \times 10^{-3} a^3 C + 8.7564 \times 10^{-7} a^6 C^2 \quad (18)$$

The complete formula for the activity coefficient of a uni-univalent strong electrolyte in aqueous solution at 25° is thus

$$\log_{10} f_\pm = -0.5059 \frac{\sqrt{C}}{1 + \frac{a}{3.042}\sqrt{C}} + 1.10313 \times 10^{-3} a^3 C + 8.7564 \times 10^{-7} a^6 C^2 \quad (19)$$

Such a formula may be expected to hold for values of a large enough to make the approximations involved in the derivation of the D. H. term acceptable. For uni-univalent electrolytes a should be larger than 2.

It is interesting to note that if formula (14) is applied to imperfect gases one finds that the correction to be added to the pressure $P = NkT/V$ is given by

$$P_w = -\frac{\partial F_w}{\partial V} = \frac{NkT}{V}\left[\frac{1}{2}\frac{N}{V}v + \frac{5}{32}\frac{N^2}{V^2}v^2\right] \quad (20)$$

Introducing the van der Waals covolume b

$$b = 4N \times \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{1}{2}Nv \qquad (21)$$

we find

$$P_w = \frac{NkT}{V}\left[\frac{b}{V} + \frac{5}{8}\left(\frac{b}{V}\right)^2\right] \qquad (22)$$

This formula gives precisely the first two terms derived by Boltzmann[8] by taking account of the possibility of more than two of the spheres of force surrounding the molecules intersecting one another.

III. Remarks Concerning the Dependence of Activity Coefficients on the Mean Ionic Diameter

We have drawn a set of standard curves corresponding to our formula (19) for round values of a ranging from 2 to 6 Å. in steps of 0.5 Å. These curves have been used in one of our methods of determining a empirically for various salts, as is explained in another section of this paper. It is interesting, at this place, to report the theoretical values of the concentration C for which $f_\pm$ is a minimum and those for which it has reached again the value *one*. These concentrations have been read from our standard curves and are reported in Table I.

TABLE I

CONCENTRATIONS AT WHICH $f_\pm$ IS A MINIMUM AND CONCENTRATIONS AT WHICH $f_\pm$ IS EQUAL TO UNITY, FOR VARIOUS VALUES OF THE IONIC DIAMETER a. (1–1 ELECTROLYTES)

a, Å.	C, moles/liter for $f_\pm$ minimum	C, moles/liter for $f_\pm = 1$
2.0	7.9	21.3
2.5	4.0	16.2
3.0	1.4	10.3
3.5	1.0	5.8
4.0	0.64	3.2
4.5	.36	2.0
5.0	.30	1.2
5.5	.20	0.81
6.0	.14	0.56

(8) L. Boltzmann, "Vorlesungen über Gastheorie," 1896, Vol. II, § 51; see J. H. Jeans, "The Dynamical Theory of Gases," Cambridge University Press, 3rd ed., 1921, p. 133.

In view of the often expressed opinion that constants or parameters in the various equations for activity coefficients should be determined from data corresponding to rather low concentrations, we wish to indicate that the activity coefficient is a rather insensitive function of the parameter a at low concentrations, particularly for small values of a, but that at high concentrations it becomes a very sensitive function of a.

We have of course

$$\frac{d \log f_{\pm}}{d \log a} = \frac{df_{\pm}}{f_{\pm}} \bigg/ \frac{da}{a} \cong \frac{\Delta f_{\pm}}{f_{\pm}} \bigg/ \frac{\Delta a}{a} \qquad (23)$$

Let us consider $\Delta a = 0.5$ Å. with $a = 2$ Å. We have then $\Delta \log f_{\pm} = \log f_{\pm} (2.5) - \log f_{\pm}(2.0)$. The percentage variation of a is $0.5/2.25$ or 22%. The corresponding variations of $\log f_{\pm}$, calculated according to our formula (19), are reported in Table II. In the same manner we have calculated the variations of $\log f_{\pm}$ corresponding to $\Delta a = 0.5$ Å. with $a = 4$ Å. In this case the percentage variation of a is 12%. The variations of $\log f_{\pm}$ are reported in the second half of Table II. These figures are very illuminating and show that, if one uses a formula with a as single parameter, the choice of the best empirical value for this parameter should be based, to a large extent, on data at high concentrations. We have devised, for this purpose, a method derived from the theory of least squares. Another striking proof of the lack of sensitivity of $f_{\pm}$ toward a change in a in the dilute range is that afforded by the curves of Fig. 1 which represent the variation of $\log f_{\pm}$ with a for various round concentrations. It will also be shown in another section of this paper that, when

TABLE II

VARIATIONS OF LOG $f_{\pm}$ CORRESPONDING TO VARIATIONS OF 0.5 Å. IN a, FOR $a = 2$ AND $a = 4$ Å.

C, moles per liter	Log $f_{\pm}$ (2)	Log $f_{\pm}$ (2.5)	$\Delta f_{\pm}/f_{\pm}$, %
0.001	−0.01566	−0.01559	0.007
.01	− .04738	− .04658	.080
.1	− .13156	− .12525	.631
1	− .29636	− .26025	3.611
2	− .35285	− .29555	5.730
5	− .41237	− .30708	10.529
10	− .42575	− .25084	17.491
	Log $f_{\pm}$ (4)	Log $f_{\pm}$ (4.5)	
0.001	−0.01529	−0.01507	0.022
.01	− .04400	− .04207	0.193
.1	− .10589	− .09143	1.446
1	− .14436	− .03980	10.456
2	− .09464	+ .11530	20.994
5	+ .15555	+ .78954	63.399
10	+ .75450	+2.48895	173.445

a has been determined from data in the concentrated range, very accurate values of $f_{\pm}$ can be calculated for the dilute range, while the opposite procedure in which a values are derived from data in the dilute range gives sometimes very erratic results.
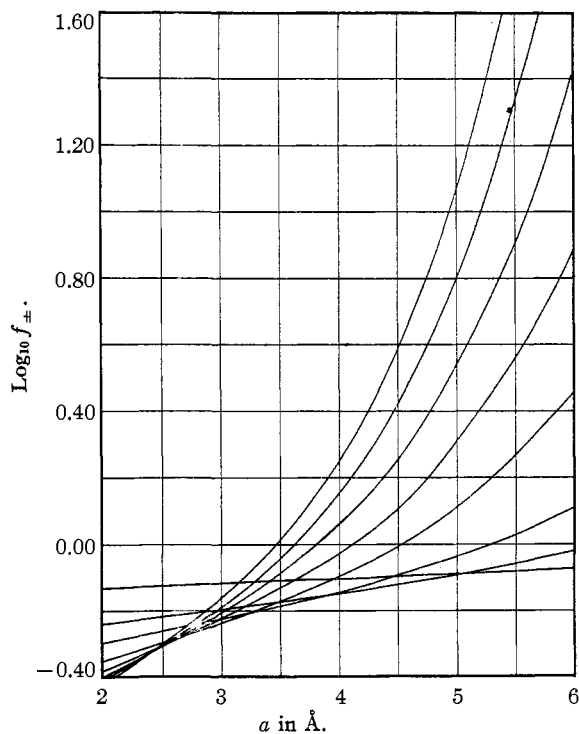

Fig. 1.—Logarithms of activity coefficients plotted against the mean ionic diameter for various round concentrations (6, 5, 4, 3, 2, 1, 0.5 and 0.1 molar from right-hand top to right-hand bottom).

IV. Determination of the Mean Ionic Diameter by the Method of Least Squares

The first step in the determination of the parameter a of a given salt consists of solving the seventh-degree equation in a corresponding to our formula (19) for some particular concentration. Only one of the solutions of this equation has physical significance and is considered as a first approximation to the exact value of a. We then calculate, for a series of round concentrations from 0.1 molar up to 4 or 5 molar, the residuals v_i defined by

$$v_i = \log \overline{f_i} - \log f_i + (\partial \log f_i/\partial \overline{a}) \Delta \overline{a} \qquad (24)$$

in which f_i is the activity coefficient calculated by our formula (19) for the approximate value $\overline{a}$ of a, f_i is the experimental activity coefficient and $\Delta \overline{a}$ the correction to be applied to $\overline{a}$. We then calculate the sum

$$S = \sum_{i=1}^{i=r} v_i^2 \qquad (25)$$

r being the number of experimental points considered, and we minimize it by the condition

$$\partial S / \partial \Delta \bar{a} = 0 \qquad (26)$$

from which we deduce

$$\Delta \bar{a} = \frac{\sum_{i=1}^{i=z} (\log f_i - \log \bar{f}_i) x_i}{1.539 \sum_{i=1}^{i=r} x_i^2} \qquad (27)$$

where x_i is given by

$$x_i = C_i \left[\frac{1}{(3.042 + \bar{a} \sqrt{C_i})^2} + 2.150 \times 10^{-8} \bar{a}^2 + 0.3413 \times 10^{-8} \bar{a}^{-8} C_i \right] \qquad (28)$$
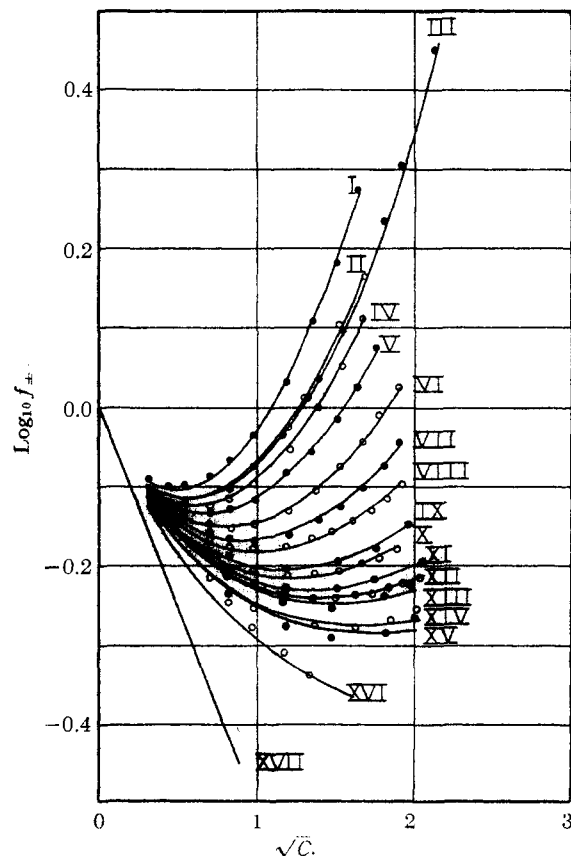

Fig. 2.—Activity coefficients of alkali halides and hydrochloric acid. The solid lines represent predicted values. The open circles represent experimental points for the even numbered salts. The solid circles represent experimental points for the odd numbered salts: I, LiI; II, LiBr; III, HCl; IV, LiCl; V, NaI; VI, NaBr; VII, NaCl; VIII, KI; IX, KBr; X, KCl; XI, RbCl; XII, RbBr; XIII, RbI; XIV, CsCl; XV, CsBr; XVI, CsI; XVII, Debye–Hückel limiting slope.

V. Application of the Theory to the Alkali Chlorides, Bromides and Iodides

The activity data used for our calculations are those of Robinson.[9] The activity coefficients γ corresponding to molalities m are converted into the rational ones $f_{\pm}$ by the well-known formula

$$\log f_{\pm} = \log \nu + \log (1 + 0.018 \nu m) \qquad (29)$$

and the molalities are transformed into volume concentrations by means of the density data. The weighted a's obtained by the method described above for the chlorides, bromides and iodides of lithium, sodium, potassium, rubidium and cesium in aqueous solution at 25° are given in the second column of Table III. On Fig. 2 we give the log $f_{\pm}$ curves corresponding to these weighted a's, and the experimental log $f_{\pm}$'s, indicated by circles, are seen to be in close agreement with these curves except in the case of cesium bromide and cesium iodide, for which appreciable departures occur.[10] It is to be noted that, particularly in the case of cesium iodide, with $a = 2.067$ Å., we are in a range of a values to which the Debye–Hückel theory is not strictly applicable. Improvements would probably be noticed if the Debye–Hückel term in our formula (19) were corrected according to the methods suggested by Bjerrum[11a] and by Gronwall, La Mer and Sandved.[11b]

Besides the a's calculated by the method of least squares, we have also determined, for a number of round concentrations ranging from 0.1 to 4–5 molar, the a's which give exact agreement with the theory. For this purpose we have used the curves of Fig. 1 from which the a's are directly read. They are reported in the third column of Table III (average values and average deviations). The results are indeed remarkable, with the sole exception of those for cesium iodide. In the last column of Table III we give the sums of the standard ionic radii for the crystals on the basis of Pauling's[12] data. We notice that, for the salts of lithium and sodium,

(9) R. A. Robinson and D. A. Sinclair, THIS JOURNAL, 56, 1830 (1934); R. A. Robinson, ibid., 57, 1161 (1935); see also O. Redlich and P. Rosenfeld, activity data in Landolt–Börnstein–Roth Tables, Dritter Ergänzungsband, Verlag von Julius Springer, Berlin. 1936, pp. 2138–2171.

(10) We also give on Fig. 2 the curve for hydrochloric acid, which almost coincides with that for lithium bromide. This case will be analyzed further in another communication.

(11) (a) N. Bjerrum, Det. Kgl. Danske Vidensk. Selsk. Math.-fysik. Medd., VII, No. 6 (1926); (b) T. H. Gronwall, V. K. La Mer and K. Sandved, Physik. Z., 29, 358 (1928).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 338.

the a's in solution are larger than the sums of the standard crystalline radii, undoubtedly on account of hydration, which is relatively more important for the lithium than for the sodium salts. With the potassium salts, a in solution is practically equal to the sum of radii in the crystal, while for the rubidium and cesium halides, the a's in solution are smaller than the sums of the standard crystalline radii.

TABLE III
MEAN IONIC DIAMETERS OF THE ALKALI CHLORIDES, BROMIDES AND IODIDES IN AQUEOUS SOLUTION AND SUMS OF THE STANDARD CRYSTALLINE RADII

Salts	a least squares, Å.	a for exact agreement, Å.	Sums of ionic radii in crystal, Å.
LiCl	4.544	4.48 ± 0.05	2.413
LiBr	4.738	4.63 ± 0.10	2.558
LiI	5.064	5.08 ± 0.02	2.775
NaCl	3.727	3.79 ± 0.09	2.764
NaBr	3.989	4.01 ± 0.04	2.909
NaI	4.308	4.29 ± 0.02	3.126
KCl	3.218	3.29 ± 0.07	3.137
KBr	3.300	3.39 ± 0.09	3.282
KI	3.551	3.67 ± 0.13	3.499
RbCl	3.061	3.07 ± 0.03	3.290
RbBr	2.980	3.00 ± 0.03	3.435
RbI	2.914	2.92 ± 0.03	3.652
CsCl	2.719	2.65 ± 0.07	3.462
CsBr	2.653	2.58 ± 0.07	3.607
CsI	2.067	2.26 ± 0.23	3.824

It seems reasonable to assume that the ions of the three potassium salts are unhydrated, or practically so, and that they can come into exact contact without deformation, since the differences $a - b$, in which b designates the sum of the standard ionic radii, are 0.081, 0.018 and 0.052 Å. for the chloride, bromide and iodide, respectively. It is then also logical to assume, at least as a working hypothesis, that the three halide ions are unhydrated in all these alkali halide solutions. Subtracting from the a's the standard crystalline radius of the negative ion we get the figures of the second column of Table IV.

We see that the resulting radii for Li$^+$ in the three halides are practically the same, showing that the amount of hydration, which can be characterized by the quantity

$$h_+ = a - (r_+ + r_-) \qquad (30)$$

given in the third column of Table IV, is constant for the three salts. We have a similar situation for the Na$^+$ ion. The h_+'s values for K$^+$ can probably be neglected, as assumed above. For the three rubidium salts we get negative values of h_+, but the differences $a - r_-$ are all positive.

TABLE IV
IONIC RADII OF THE POSITIVE IONS IN SOLUTIONS OF THE ALKALI CHLORIDES, BROMIDES AND IODIDES

Salts	$a - r_-$, Å.	$a - (r_- + r_+)$, Å.
LiCl	2.738	2.131
LiBr	2.787	2.180
LiI	2.896	2.289
NaCl	1.921	0.963
NaBr	2.038	1.080
NaI	2.140	1.182
KCl	1.412	0.081
KBr	1.349	.018
KI	1.383	.052
RbCl	1.255	− .229
RbBr	1.029	− .455
RbI	0.746	− .738
CsCl	.913	− .743
CsBr	.702	− .954
CsI	− .101	−1.757

This could be explained by assuming that, at closest approach, the positive and negative ions penetrate each other, the center of the positive ion being outside the negative one. The difference represents the distance between the center of the positive ion and the surface of the negative one. We have the same situation with cesium chloride and cesium bromide, but with cesium iodide $a - r_-$ is negative, showing that, on the basis of the above suggestion, the center of the positive ion is now inside the negative ion, at 0.101 Å. from the surface of the latter. We have represented on Fig. 3 the variation of a with the
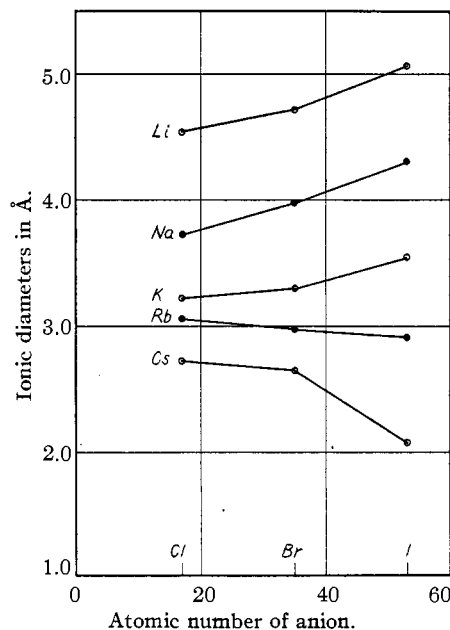

Fig. 3.—Ionic diameters of alkali salts in aqueous solutions plotted against the atomic number of the anion.

atomic number of the negative ion for each alkali metal and on Fig. 4 the variation of a with the atomic number of the positive ion for each halogen.
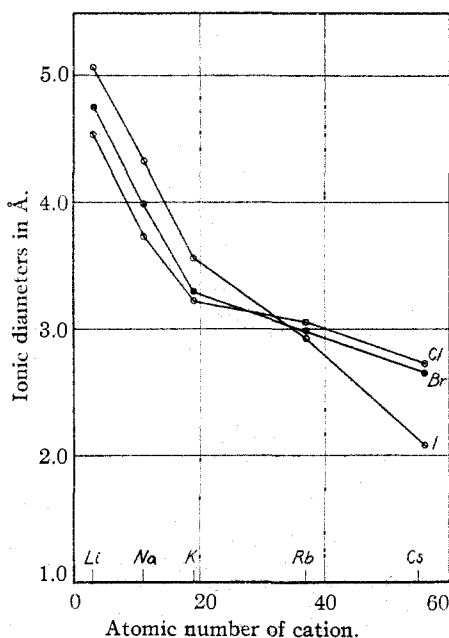

Fig. 4.—Ionic diameters of alkali salts in aqueous solutions plotted against the atomic number of the cation.

VI. Activity Coefficients in the Dilute Range. Concluding Remarks

We have calculated the activity coefficients of 0.001 and 0.01 molar solutions of the fifteen halides

TABLE V

ACTIVITY COEFFICIENTS OF DILUTE ALKALI CHLORIDES, BROMIDES AND IODIDES

Salts	$C = 0.001$ $f_\pm$ exptl.	$f_\pm$ calcd.	$C = 0.01$ $f_\pm$ exptl.	$f_\pm$ calcd.	Ref.
LiCl	0.9631	0.9656	0.8954	0.9057	13
LiBr	.9663	.9658	.9096	.9066	13
LiI		.9658		.9078	
NaCl	.9659	.9652	.9063	.9026	13
NaBr	.966	.9654	.9141	.9037	13
NaI	.966	.9656	.917	.9049	14
KCl	.9652	.9652	.9026	.9007	13
KBr	.9651	.9652	.9037	.9012	13
KI	.965	.9652	.905	.9020	15
RbCl		.9649		.8997	
RbBr		.9649		.8999	
RbI		.9649		.8997	
CsCl		.9649		.8991	
CsBr		.9649		.8989	
CsI		.9645		.8968	

(13) G. Scatchard and S. S. Prentiss, THIS JOURNAL, **55**, 4355 (1933).
(14) G. Karagunis, A. Hawkinson and G. Damköhler, Z. physik. Chem., **A151**, 433 (1930).
(15) Landolt–Börnstein–Roth Tables, ref. 9.

using the weighted a's of Table III, which were all determined from data at concentrations larger than 0.1 molar. For eight of the salts experimental values are available and the agreement is surprisingly good, as shown in Table V. As noted above already, the reverse procedure, by which a would be calculated from these data in the dilute range, gives erratic results (a becoming sometimes as large as 7 Å.). Inspection of Fig. 1 and our remarks of section III should make this point perfectly clear.

We wish to point out that our one-parameter formulation leads to better agreement with the data than the interesting but more complicated treatment proposed by Scatchard.[16] We believe that the effect of the ionic charges on the dielectric constant of the solution and the other interactions analyzed by Scatchard are implicitly contained in our equation and that they all affect the value of a. Scatchard uses the ionic radii corresponding to the crystal lattices reported by Pauling in 1928,[17] and it should be pointed out that these values are somewhat smaller than the corrected ones recently published by Pauling.[12] It also should be noted that our treatment constitutes, at least for the salts discussed in the present paper, a definite improvement on the only other one-parameter treatment so far proposed, namely, that of Guggenheim,[5] whose range of applicability is limited by an ionic strength of 0.1.

We already have obtained a number of promising results with other 1–1 electrolytes and with some 2–1, 2–2 and 3–1 electrolytes, as well as with some non-electrolytes, which appear to follow our equation (19) when the electrostatic term is left out. These results and other work at present in progress will be reported in subsequent papers.

Summary

1. The problem of expressing the activity coefficients of strong electrolytes as functions of a single parameter, the distance of closest approach between positive and negative ions or mean ionic diameter, is stated.

2. The van der Waals or covolume terms in the activity coefficient formula are derived on the basis of a theory due to Ursell. A term proportional to the volume concentration and to the cube of the distance of closest approach, and another one proportional to the square of the vol-

(16) G. Scatchard, Chem. Rev., **19**, 309 (1936).
(17) L. Pauling, THIS JOURNAL, **50**, 1036 (1928); Z. Krist., **67**, 377 (1928).

ume concentration and to the sixth power of the distance of closest approach, are added to the Debye–Hückel expression for the logarithm of the activity coefficient.

3. It is shown that only at high concentrations do the activity coefficients become sufficiently sensitive functions of the distance of closest approach to make the determination of this parameter really precise.

4. The determination of this parameter by the method of least squares is described.

5. The theory is applied to the alkali chlorides, bromides and iodides with remarkable suc-

cess. A set of mean ionic diameters is obtained, and various remarks as to the extent of hydration, penetration of ions at contact, etc., are derived from a comparison of these diameters with the sums of the standard crystalline radii.

6. Activity coefficients in 0.001 and 0.01 molar solutions are calculated with the weighted mean ionic diameters obtained at high concentrations. In eight cases out of fifteen comparison with experimental values is possible and shows more than satisfactory agreement.

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The Bromination of 4-Phenylphenyl Acetate

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In previous reports it was shown that although the bromination of 4-phenylphenol results in substitution at a position ortho to the hydroxyl group, when the benzenesulfonate[1] or the benzoate[2] of the phenol is brominated, the substitution occurs at the position in the molecule most remote from the ester linkage (viz., p'). The study of the introduction of bromine into the esters of 4-phenylphenol has been extended now to 4-phenylphenyl acetate, which is analogous to the benzenesulfonate and the benzoate previously considered.

It was suggested in an earlier report[2] that perhaps steric hindrance is responsible for the change in directive influence when hydroxyl is modified to benzenesulfonyloxy or benzoyloxy. In the work here reported (see Chart I for the outline) the hydroxyl of 4-phenylphenol (I) was replaced by the acetyloxy group. On the basis of the calculations of Latimer and Porter[3] the acetyloxy group of compound II should possess the same residual charge as the benzoyloxy group in one of the compounds previously studied. The acetyloxy group is, however, much smaller than the benzoyloxy group and should be expected to exert less steric effect. Therefore it was considered possible that the bromination of 4-phenylphenyl acetate (II) might result in substitution in a position ortho with respect to the acetyloxy group. This was realized; it was found that the first bromine atom

to enter 4-phenylphenyl acetate (II) gave rise to 2-bromo-4-phenylphenyl acetate (IV). Furthermore, under conditions only slightly different from those used in the preparation of compound IV and in the earlier studies,[1,2] a second atom of bromine entered the ester molecule (II) in the same relative position as in the case of the phenol (I), viz., the second ortho position; thus 2,6-dibromo-4-phenylphenyl acetate (VI) was formed.

A bromine substitution product of compound II, 4-(4-bromophenyl)-phenyl acetate (IX), isomeric with compound IV obtained by direct bromination of the acetate (II) was prepared by the acetylation of a phenol (VIII) of known structure. The two isomers had distinctly different physical properties.

The experimental steps and the proofs of structure of the compounds are outlined in Chart I, and the details of procedures are given in the Experimental Part.

Experimental Part

4-Phenylphenyl Acetate (II).[4]—This compound was prepared in almost quantitative yield by gently refluxing for three hours one mole of 4-phenylphenol (I) and 0.25 mole of anhydrous sodium acetate in an excess of acetic anhydride. The reaction mixture was allowed to cool, poured into ten volumes of water, and permitted to stand overnight. The ester was collected by filtration and recrystallized from methanol. The colorless, irregular crystals melted between 87 and 88°.

2-Bromo-4-phenylphenyl Acetate (IV).—Fifteen grams of 4-phenylphenyl acetate (II) was dissolved in 30 ml. of

(1) Hazlet, THIS JOURNAL, **59**, 1087 (1937).
(2) Hazlet, Alliger and Tiede, ibid., **61**, 1447 (1939).
(3) Latimer and Porter, ibid., **52**, 206 (1930).
(4) Kaiser, Ann., **257**, 95 (1890).