the constituents which give rise to an appreciable solvent conductance probably have sizable, weak Wien effects, the accuracy claimed is not high.

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NEW HAVEN, CONN.

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[CONTRIBUTION NO. 1095 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# A Correction for the Computed High Field Conductance of Strong 2–2 Electrolytes

BY FREDERICK E. BAILEY, JR., AND ANDREW PATTERSON, JR.

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The high field conductance of 2–2 electrolytes such as magnesium and zinc sulfates is found to lie appreciably above the theoretical values computed with aid of the Onsager–Wilson theory. This fact is attributed to the presence of ion pairs in the otherwise strong electrolyte; these ion pairs behave like a weak electrolyte under high field excitation. It is shown that a combination of the Onsager theories for the high field conductance of strong and of weak electrolytes gives rise to a satisfactory agreement between experiment and theory.

The results of several investigators[1–3] indicate that the high field conductance of magnesium or zinc sulfate as a function of field falls appreciably higher than the values computed from the equation of Onsager and Wilson[4–6]

$$\Lambda_x = \Lambda^0 - \frac{|e_j|^2\kappa\Lambda^0}{2DkT}\,g(x) - \frac{96500k|e_j|2\kappa}{6\sqrt{2\pi\eta}300}\,f(x) \qquad (1)$$

The assumption of ion pairs in 2–2 electrolytes is consonant with the interpretation of a number of phenomena, among which the diffusion of zinc sulfate in aqueous solution[7] may be mentioned as a recent example. We may demonstrate that the present case is no exception.

We assume that ion pairs behave as in weak electrolytes under the influence of high potential gradients, estimate from low field conductance data the concentration of ion pairs and strong electrolyte ions remaining in solution, and combine the results of the theories of Onsager for strong[4,5] and for weak[8] electrolytes to obtain a corrected set of theoretical high field conductance values. This is accomplished by computing the degree of dissociation of the 2–2 electrolyte as a function of field with aid of Onsager's theory for weak electrolytes[8] and using this varying degree of dissociation to correct the usual high field conductance equation of Onsager and Wilson, as will be noted in the following section.

## Theoretical Calculations

Onsager's function F($b$)[8] is computed at selected values of field from the expression

$$F(b) = \frac{K(X)}{K(0)} = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \frac{b^5}{2700} + \cdots \qquad (2)$$

where

$$b = \frac{z_1^2 z_2^2(\Lambda_1 + \Lambda_2)}{z_2\Lambda_1 + z_1\Lambda_2} \times \frac{[X]e^3}{2Dk^2T^2} \qquad (3)$$

These values are tabulated in column 2 of Table I as a function of field, column 1. These quantities are used to calculate $K(X)$ as defined by Onsager,[8] using the quantities for $K(0)$ found on page 147 of Harned and Owen[5]; for magnesium sulfate $K(0) = 0.0063$; for zinc sulfate, $K(0) = 0.0049$. The quantity $\alpha$, the degree of dissociation, is computed at zero field from the relation

$$K(0) = \frac{c\gamma_\pm^2}{1-\alpha_0} \text{ or } \alpha_0 = \frac{1 - c\gamma_\pm^2}{K(0)} \qquad (4)$$

The numerical value for $\gamma_\pm$ of 0.90 is used for magnesium sulfate and 0.89 is used for zinc sulfate; these quantities were estimated in each case from a plot of $\gamma_\pm$ *versus* $c$ using data from Harned and Owen[5], pp. 426–427. At fields other than zero, the degree of dissociation is calculated from the mass action law with the assumption that $\gamma_\pm$ is unity. This is, of course, an approximation; presumably $\gamma_\pm$ approaches unity with increasing field. (The effect of this approximation is discussed in the following section.)

$$K(X) = \frac{c\alpha^2}{1-\alpha} \text{ or } \alpha = 1 - \frac{c}{K(X)} + 2\left(\frac{c}{K(X)}\right)^2 - 5\left(\frac{c}{K(X)}\right)^3 + \cdots \qquad (5)$$

Values of $K(X)$ at increasing field are obtained from equation (2). The computed values of $\alpha$ are tabulated in column 3 of Table I.

The values of $\alpha c$ and $(\alpha c)^{1/2}$ are then computed for the same values of field corresponding to the values of $\alpha$ used, and these quantities $(\alpha c)^{1/2}$ are employed to compute $\kappa$ according to the relation

$$\kappa = \left(\frac{4\pi e^2 N2}{1000DkT}\right)^{1/2} z\,(\alpha c)^{1/2} \qquad (6)$$

With these numerical values of $\kappa$ at increasing field, it is possible to compute $x$, the argument of Onsager and Wilson, since $x$ is a function not only of field but of $\kappa$ as well

$$x = Xze/kT\kappa \qquad (7)$$

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(1) M. Wien, *Ann. Physik*, **85**, 795 (1928).

(2) J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, accepted for publication, December 1952.

(3) F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4426 (1952).

(4) W. S. Wilson, Dissertation, Yale University, 1936.

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 2nd ed., 1950, pp. 95–114, 214–217.

(6) The symbols used throughout this paper are those of Harned and Owen,[5] as follows: $\Lambda_X$, the equivalent conductance of the electrolyte at finite concentration and at field $X$; $\Lambda^0$, the equivalent conductance of the electrolyte at infinite dilution; $e_j$, the charge carried by the $j$ ion (with sign); $\kappa$, the reciprocal of the radius of the ionic atmosphere in the Debye–Hückel–Onsager theories; $D$, the dielectric constant of the solution; $k$, the Boltzmann constant; $T$, the absolute temperature; f($x$) and g($x$), Wilson's functions[5]; $\eta$, the viscosity of the solution; $K(X)$, the dissociation constant at field $X$; $K(0)$, the dissociation constant at field $X = 0$; $z_j$, the number of unit charges carried by the $j$ ion (with sign); $\Lambda_j$, the equivalent ionic conductance of the $j$ ion; $X$, the field strength in e.s.u.; $e$, the electronic charge in e.s.u.; $\gamma_\pm$, the mean molar ionic activity coefficient; $\alpha$, the degree of dissociation of the electrolyte under field $X$; $\alpha_0$, the degree of dissociation of the electrolyte under zero field; $S_\Lambda$, the limiting slope of the equation for the equivalent conductance of an electrolyte as a function of concentration; $S_{\Lambda x}$, the limiting slope at field $X$ as calculated from Wilson's functions[5]; $c$, the concentration in moles per liter; and $\Delta\lambda/\lambda_{x=0}$, the per cent. increase in conductance, $\lambda_x - \lambda_{x=0}$, relative to the conductance at zero field, $\lambda_{x=0}$.

(7) H. S. Harned and R. M. Hudson, THIS JOURNAL, **73**, 3781 (1951).

(8) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

The quantity $X$ has the value $X = V/300$ if $V$ is in volts/cm.

One is now in a position to employ the following relation to compute the conductance at a given field, $\Lambda_x$

$$\Lambda_X = \alpha \left\{ \Lambda^0 - \left( \frac{3\alpha^* \Lambda^0}{2 - \sqrt{2}} \mathrm{g}(x) + \frac{\beta^*}{\sqrt{2}} \mathrm{f}(x) \right) (\alpha c)^{1/2} \right\} \quad (8)$$

Reference may be made to Harned and Owen[5] who have tabulated $\alpha^*$, $\beta^*$, $\mathrm{f}(x)$ and $\mathrm{g}(x)$. In this equation the quantities are equivalent to the expression

$$\Lambda_X = \alpha \{ \Lambda^0 - \mathcal{S}_{\Lambda X} (\alpha c)^{1/2} \} \quad (9)$$

for the conductance of an electrolyte at high dilution where the fraction of the electrolyte present as ions is $\alpha$ and the mean ionic concentration is $\alpha c$. Column 4 of Table I is so headed, it being understood that the computation has been made using equation (8), that $\alpha$ in this case refers to a degree of dissociation at field $X$, and that the slope, $\mathcal{S}_{\Lambda X}$, is also a function of field.

To obtain the usually plotted quantity $\Delta\lambda/\lambda_0$ it is necessary only to take the differences between the conductances at zero field and those at increasing fields and to divide the differences by the conductance at zero field. These quantities are tabulated in column 5 of Table I. The fractional change in conductance of the reference potassium chloride solutions is taken from the paper of Bailey and Patterson[3] for the magnesium sulfate calculation, and from Gledhill and Patterson[2] for the zinc sulfate calculation.

TABLE I

CORRECTED ONSAGER–WILSON THEORY FOR THE HIGH FIELD CONDUCTANCE OF MAGNESIUM AND ZINC SULFATE SOLUTIONS RELATIVE TO POTASSIUM CHLORIDE AT 25°.

| Field, kv./cm. | F(b) | $\alpha$ | $\alpha\{\Lambda^0 - \mathcal{S}_{\Lambda x} (\alpha c)^{1/2}\}$ | $\frac{\Delta\lambda,}{\lambda_x = 0}$ corr., % | $\frac{\Delta\lambda,}{\lambda_{x0}}$ KCl, % | $\frac{\Delta\lambda,}{\lambda_x = 0}$ rel., % |
|---|---|---|---|---|---|---|
| $MgSO_4$, 1.390 × $10^{-4}$ molar<br>$\Lambda^0 = 133$ | | | $KCl$, 2.335 × $10^{-4}$ molar<br>$\Lambda^0 = 149.85$ | | | |
| 0 | 1 | 0.9821 | 125.06 | 0.000 | 0.000 | 0.000 |
| 10 | 1.114 | .9810 | 125.33 | 0.217 | .036 | 0.181 |
| 20 | 1.238 | .9828 | 126.15 | 0.869 | .101 | 0.768 |
| 40 | 1.512 | .9858 | 127.29 | 1.782 | .203 | 1.579 |
| 80 | 2.185 | .9901 | 128.52 | 2.763 | .309 | 2.454 |
| 100 | 2.594 | .9916 | 128.89 | 3.058 | .339 | 2.719 |
| 200 | 5.585 | .9964 | 129.92 | 3.888 | .414 | 3.474 |
| $ZnSO_4$, 1.640 × $10^{-4}$ molar<br>$\Lambda^0 = 133$ | | | $KCl$, 2.88 × $10^{-4}$ molar<br>$\Lambda^0 = 149.85$ | | | |
| 0 | As | 0.9686 | 123.52 | 0.000 | 0.000 | 0.000 |
| 20 | above | .9743 | 124.60 | 0.876 | .098 | 0.778 |
| 40 | | .9788 | 125.98 | 1.993 | .208 | 1.785 |
| 80 | | .9851 | 127.53 | 3.248 | .328 | 2.920 |
| 100 | | .9874 | 128.02 | 3.646 | .362 | 3.284 |
| 200 | | .9941 | 129.36 | 4.730 | .454 | 4.276 |

## Discussion

Figure 1 is a plot of the experimental data of refs. 2 and 3 for zinc and magnesium sulfates with the corrected theoretical data of Table I drawn for comparison. Whereas the theory of Onsager and Wilson, uncorrected for the weakness of the two electrolytes, gives rise to differences between the percentages of the experimental and theoretical curves of 1.5 for magnesium sulfate and 1.7 for zinc sulfate, there is considerably better agreement between the corrected theoretical values and experiment. In this case the differences are reduced to 0.2 and 0.4 for the magnesium and zinc sulfates, respectively, and the theory lies above experiment not below. These numerical differences refer to the values at 200 kv./cm. The position of the corrected curves is principally dependent upon the choice of $K(0)$. The numerical value of $K(0)$ may vary considerably, depending on the mode of extrapolation of the low field conductance data. For zinc sulfate, the Shedlovsky extrapolation (see ref. 5) leads to the value 0.0049 which we have employed here, while the Fuoss extrapolation leads to the value 0.0052. These two values differ by 6%. As it happens, higher values of $K(0)$ would improve the agreement of theory and experiment for both of our curves. Although the agreement between our corrected theory and experiment is not perfect, and it is realized that there are difficulties in interpreting low field conductance data to obtain a $K(0)$, nevertheless the agreement observed suggests a degree of physical reality in the model of ion pair-ion equilibrium as the source of weakness in 2–2 electrolytes.

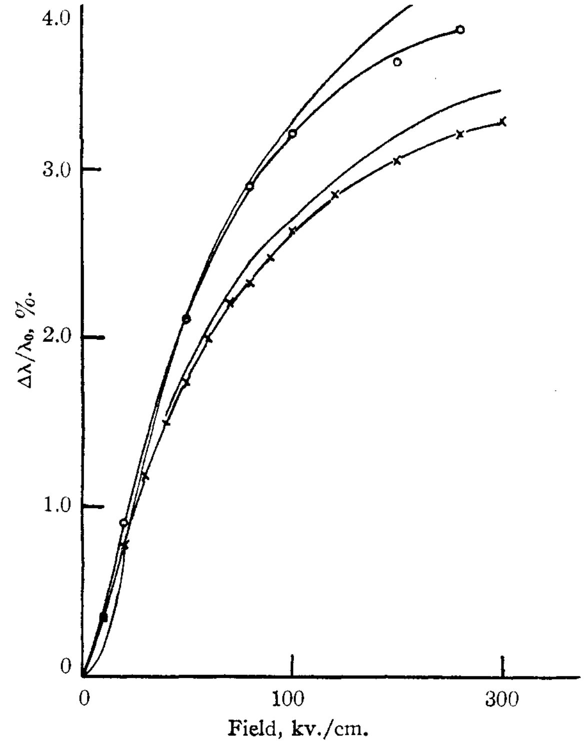

Fig. 1.—The high field conductance of zinc sulfate, above, O; and magnesium sulfate, below, ×; relative to potassium chloride at 25°. The solid lines in each case are the corrected theoretical curves.

At low fields, the theory falls below the experimental results; this is undoubtedly due to the assumption of unity for the activity coefficient at fields other than $X = 0$; this assumption is the more serious the lower the field, but becomes unimportant at higher fields as $\gamma_\pm$ approaches unity.

It was found by Bailey and Patterson[3] that the high field conductance of magnesium sulfate, when plotted as the fractional increase of conductance with field, $\Delta\lambda/\lambda_0$, was essentially invariant with temperature over the range 5–55°. We may note from the above that $F(b)$, equation (2), is not overly temperature sensitive, since $b$ changes only about 10% over the temperature range 5–55° for a 2–2 electrolyte. Furthermore, in the statement of Bjerrum's theory[9] of ion pair formation the factors $D$ and $T$ appear together and to the same power

[9] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926); also ref. 5, p. 122.

both in the equation itself and in $Q(b)$

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1z_2|e^2}{kDT}\right)^3 Q(b) \qquad (10)$$

where

$$b = |z_1z_2|e^2/aDkT \qquad (11)$$

As the temperature rises, the dielectric constant decreases; over the temperature range 5–55° the product varies only about 6%. Although the theoretical values employed in ref. 3 were computed from the uncorrected Onsager–Wilson theory, and it would be impossible to carry out the correction made in this paper because of lack of data for $K(0)$ at temperatures other than 25°, the combination of factors just mentioned makes it improbable that the term $\Delta\lambda/\lambda_0$ would change appreciably over the temperature range investigated, even though the actual conductance of the solutions varies considerably.

We may conclude from the consistency of the experimental data of ref. 3 that the value of $K(0)$ changes probably less than 10% from the values employed at 25°. This is within the precision with which the equilibrium constant may be determined from a single set of conductance data.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS COMPANY]

# Some New Uranium Complexes[1]

BY JOHN T. BARR AND CHARLES A. HORTON

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A study has been made of the action of organic bases, acidic complexing agents and amino acids upon organic solutions of uranium compounds. The type of product which was obtained was a function of both the oxidation state of the uranium and of the type of complexing agent. Organic bases precipitated uranium ammines. Acidic complexing agents did not form identifiable products, although spectrophotometric evidence indicated that enolized 1,3-diketones complexed to some extent. The addition of an external base to solutions of a uranium compound and an acidic complexing agent precipitated mixed complexes containing both organic and inorganic groups. Complexing agents which themselves contained an amino group reacted readily with uranyl salts to form inner complexes, and with uranium(IV) salts to form mixed complexes. The infrared absorption spectra of 9 of the complexes and ammines are presented, and a mechanism is proposed to account for the formation of the complexes.

It has been found in this work that many of the same complexing agents which are known to coördinate uranium in aqueous media also react with uranium compounds in non-aqueous solution. However, many of the products which are formed in non-aqueous solution differ greatly from those formed in aqueous media.

A typical method of preparation of inner complexes consists of the cautious addition of an alkali to a solution of a bidentate complexing agent and a uranium salt in water, thus obtaining a precipitate of the complex.[2] When, in this work, the same method was extended to non-aqueous systems, with the substitution of an amine for the alkali, and *n*-butyl acetate, or a similar oxygenated solvent for the water, a product was obtained which did not resemble an inner complex in nature. These new complexes were more soluble in water than in organic solvents. Many did not melt below 350° and a number were ionic in character, consisting of a complex cation and an inorganic anion.

The exact nature of the product was a function of the oxidation state of the uranium, and of the type of complexing agent. Organic bases alone precipitated uranyl and uranium(IV) salts as ammines. Complexing agents which contained only acidic functional groups (*i.e.*, salicylic acid) did not form precipitates with either type uranium salts, although spectrophotometric evidence indicated partial reaction in some cases. Presumably, the product was an organic-soluble inner complex. The addition of an organic base to solutions of uranium compounds and acidic bidentate complexing agents in an organic solvent gave, with uranyl compounds, an electrolyte in which one of the inorganic anions had been replaced by a bidentate organic anion in the coördination sphere of the uranyl ion. One molecule of the organic base and one molecule of water completed the normal coördination number of 4 for the uranyl ion. The second inorganic anion was ionic. Two inorganic anions were displaced by bidentate groups from the uranium(IV) salts, and two molecules of the base were combined in the complex. The remaining two inorganic anions are thought to have been included in the coördination sphere of the uranium, in order to satisfy the normal coördination number of 8 for the uranium(IV) ion. However, the inorganic anions were very readily hydrolyzed by aqueous solutions.

Complexing agents which themselves contained a basic group (N-phenylglycine, quinaldinic acid) gave immediate precipitates with uranium solutions. Uranyl compounds precipitated as aquated inner complexes. Uranium(IV) compounds gave products similar to those described in the previous paragraph except that the two basic coördinating groups were replaced by a third molecule of the amino acid.

Uranium(V) and (VI) chlorides were precipitated from carbon tetrachloride solution by bases and amino acids, to give products which were stable to storage under the solvent for short periods, and which underwent immediate hydrolysis upon ex-

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(1) This paper is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company at Oak Ridge, Tennessee.

(2) H. Gilman and R. G. Jones, Report AECD-2613, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. Declassified September 30, 1949.