[CONTRIBUTION NO. 1086 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The High Field Conductance of Magnesium Sulfate Relative to Potassium Chloride from 5 to 55°[1]

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The high field conductance of magnesium sulfate relative to potassium chloride in aqueous solution in the concentration range 10^{-4} molar has been determined from 5 to 55° using the differential pulse transformer bridge circuit. The high field conductance when given as $\Delta\lambda/\lambda_0$ is shown not to be a significantly varying function of temperature, in accordance with the predictions of the Onsager–Wilson theory, but the results are shown to deviate consistently from the values computed with aid of this theory.

Although a quarter of a century has passed since Wien[2] announced his discovery that the conductances of electrolytic solutions do not conform to Ohm's law under the influence of high potential gradients, only one set of precise data has been presented for a symmetrical valence type strong electrolyte[3] with which it is possible to test the theory of Onsager and Wilson.[4,5] In Wien's papers the temperature was unspecified. The present paper includes data on the high field conductance of magnesium sulfate in aqueous solution, approximately 10^{-4} molar, relative to potassium chloride over the temperature range 5 to 55°.

Experimental

The experimental procedure was identical with that of Gledhill and Patterson,[6] employing a differential pulse transformer bridge circuit. All measurements were made with four-microsecond pulse duration. The salts employed were of highest quality reagent grade, purified by recrystallization. The solutions on which conductance measurements were actually made were prepared by weight dilution of suitable strong stock solutions of each salt. The strong stock solutions were analyzed by weighing suitable quantities into platinum dishes, evaporating the water, and reweighing. The details of the procedure are described by Gledhill and Patterson.[6] The temperature control was to within 0.015 at 25° and within 0.02° at all other temperatures. All temperatures were measured against a recently calibrated platinum resistance thermometer.

Results

Table I contains the experimental results as well as relative Wien effects computed from the Onsager–Wilson theory,[4,5] using the equation

$$\lambda_j = \lambda_j^0 - \frac{\epsilon^2\kappa}{2DkT}\lambda_0 g(x) - \frac{96{,}500|\epsilon|\kappa}{6\sqrt{2}\,\eta_0 300} f(x) \qquad (1)$$

The symbols are those of Harned and Owen.[5] The first column lists the field strengths employed, the next two columns contain the experimental data, and the remaining columns are for the theoretical calculations. The experimental data are given in the form of resistance at low field, which is equivalent to zero field for these electrolytes, and of resistances of the magnesium sulfate solution at increasing field. The results are reported as $\Delta\lambda/\lambda_0$, in per cent. The computations have been made in the same way as in reference 6. The Onsager–Wilson theory calculations are given in essentially the same form, as equivalent conductance at low field for the concentration and temperature employed and the computed per cent. fractional high field conductance, $\Delta\lambda/\lambda_0$. Column 4 pertains to the magnesium sulfate; column 5, to the potassium chloride. Column 6 gives the theoretical relative Wien effect for magnesium sulfate.

Figure 1 is a plot of these data. In the determination at 5° a slightly higher concentration was employed, and thus two curves are drawn both for the experimental points, above, and the theoretical values, below. The higher curves correspond to the 5° measurements.

No difficulties in the performance of the conductance cells when subjected to high field excitation or temperature cycling were observed.

TABLE I

THE HIGH FIELD CONDUCTANCE OF AQUEOUS SOLUTIONS OF MAGNESIUM SULFATE RELATIVE TO POTASSIUM CHLORIDE FROM 5 TO 55°

5°

$MgSO_4$: 1.585 × 10^{-4} molar
R_0 = 1842.5 ohms
Experimental results:

KCl: 2.512 × 10^{-4} molar
R_0 = 1754.0 ohms
Onsager–Wilson theory:
Λ^0 $MgSO_4$ = 78, Λ^0 KCl = 94.23
Λ_{x0} = 74.5 Λ_{x0} = 93.34

Field, kv./cm.	R_V $MgSO_4$	$\Delta\lambda/\lambda_0$, %	$\Delta\lambda/\lambda_0$, % $MgSO_4$	$\Delta\lambda/\lambda_0$, % KCl	$\Delta\lambda/\lambda_0$, % Rel. $MgSO_4$
10	1835.0	0.409			
20	1825.2	0.948	0.843	0.106	0.737
30	1817.3	1.387			
40	1811.5	1.711			
50	1807.0	1.964	1.678	.243	1.435
60	1803.1	2.185			
70	1799.8	2.375			
80	1798.2	2.464			
90	1795.5	2.618			
100	1793.4	2.738	2.191	.342	1.849
120	1788.5	3.016			
150	1785.3	3.207			
180	1783.0	3.337			
200	1781.0	3.453	2.536	.414	2.122

15°

$MgSO_4$: 1.391 × 10^{-4} molar
R_0 = 1584.9 ohms

KCl: 2.410 × 10^{-4} molar
R_0 = 1478.4 ohms
Λ^0 $MgSO_4$ = 104
Λ_{x0} = 99.6
Λ^0 KCl = 121.03
Λ_{x0} = 119.88

Field, kv./cm.	R_V $MgSO_4$	$\Delta\lambda/\lambda_0$, %	$\Delta\lambda/\lambda_0$, % $MgSO_4$	$\Delta\lambda/\lambda_0$, % KCl	$\Delta\lambda/\lambda_0$, % Rel. $MgSO_4$
10	1579.8	0.326	0.340	0.037	0.303
20	1572.8	0.773	0.852	.103	0.749
30	1566.7	1.162			
40	1560.9	1.541			
50	1556.9	1.802	1.610	.240	1.370
60	1552.8	2.070			
70	1551.6	2.149			
80	1547.9	2.394	1.940	.310	1.630
100	1544.1	2.645	2.089	.340	1.749
120	1540.9	2.859			
150	1537.4	3.090	2.294	.385	1.909
180	1534.0	3.321			
200	1532.6	3.412	2.410	.413	1.997

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[1] This material is taken from a dissertation submitted by F. E. Bailey, Jr., to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1952.

[2] M. Wien and J. Malsch, *Ann. Physik*, **83**, 305 (1927).

[3] M. Wien, *ibid.*, **85**, 795 (1928); *Physik. Z.*, **29**, 751 (1928).

[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., 2d ed., 1950, pp. 95–114.

[6] J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, submitted for publication, December, 1952.

TABLE I (*Continued*)

		25°			
$MgSO_4$: 1.390 × 10^{-4} molar R_0 = 1257.0 ohms			KCl: 2.335 × 10^{-4} molar R_0 = 1198.2 ohms Λ^0 $MgSO_4$ = 133 Λx_0 = 127.3 Λ^0 KCl = 149.85 Λx_0 = 148.41		
10	1252.7	0.343	0.325	0.036	0.298
20	1247.2	0.786	0.800	.101	0.699
30	1242.2	1.191			
40	1238.5	1.494			
50	1235.6	1.732	1.603	.239	1.364
60	1232.4	1.996			
70	1229.8	2.208			
80	1228.5	2.320	1.985	.309	1.649
90	1226.7	2.470			
100	1224.7	2.637	2.108	.340	1.768
120	1222.2	2.843			
150	1219.8	3.050	2.314	.387	1.927
180	1217.9	3.206			
200	1216.9	3.291	2.435	.414	2.021
		35°			
$MgSO_4$: 1.373 × 10^{-4} molar R_0 = 1030.0 ohms			KCl: 2.453 × 10^{-4} molar R_0 = 982.0 ohms Λ^0 $MgSO_4$ = 165 Λx_0 = 157.8 Λ^0 KCl = 180.41 Λx_0 = 178.57		
10	1027.0	0.292	0.314	0.034	0.280
20	1023.0	0.684	0.781	.097	0.684
30	1018.6	1.114			
40	1015.4	1.438			
50	1011.9	1.789	1.591	.240	1.351
60	1009.8	2.000			
70	1008.0	2.182			
80	1006.1	2.370	1.957	.316	1.641
90	1004.7	2.518			
100	1003.6	2.631	2.103	.327	1.756
120	1001.3	2.866			
150	998.4	3.165	2.317	.399	1.918
200	996.3	3.382	2.444	.430	2.014
		45°			
$MgSO_4$: 1.375 × 10^{-4} molar R_0 = 855.7 ohms			KCl: 2.467 × 10^{-4} molar R_0 = 829.2 ohms Λ^0 $MgSO_4$ = 199 Λx_0 = 190.3 Λ^0 KCl = 212.43 Λx_0 = 210.20		
20	848.0	0.766			
30	846.5	1.087			
50	839.2	1.823	1.591	0.238	1.353
60	838.3	2.082			
90	834.4	2.559			
100	831.8	2.729	2.108	.351	1.757
120	830.2	2.927			
150	829.3	3.183			
180	828.2	3.326			
200	827.1	3.464	2.480	.436	2.044
		55°			
$MgSO_4$: 1.369 × 10^{-4} molar R_0 = 719.0 ohms			KCl: 2.455 × 10^{-4} molar R_0 = 707.3 ohms Λ^0 $MgSO_4$ = 235 Λx_0 = 224.5 Λ^0 KCl = 245.67 Λx_0 = 243.04		
20	719.0	0.637			
40	708.3	1.504			
50			1.587	0.235	1.352
60	704.0	2.131			
80	701.9	2.436			
100	700.6	2.626	2.131	.352	1.779
120	699.0	2.861			
150	697.3	3.112			
180	695.5	3.371			
200	694.7	3.498	2.506	.439	2.067

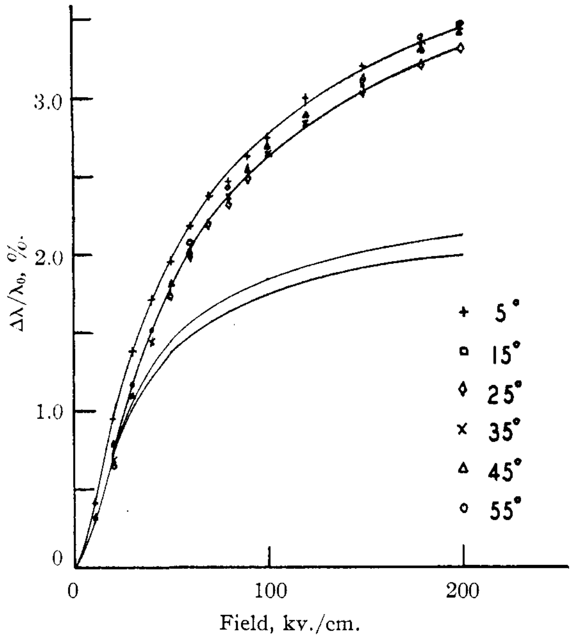

Fig. 1.—The high field conductance of magnesium sulfate relative to potassium chloride from 5 to 55°: above, experimental results: below, Onsager–Wilson theory. In both cases the higher curves are for 5°, the lower curves for 25°.

Discussion of Results

The high field conductance of magnesium sulfate relative to potassium chloride, when expressed as $\Delta\lambda/\lambda_0$, does not appear to vary significantly with temperature. The results for 5° are slightly higher than the values at other temperatures, but this is a result of the higher concentration employed at that temperature. There is some evidence that the values at 25° are slightly lower than those at temperatures both below and above 25°. The figures computed from the Onsager–Wilson theory similarly show no significant dependence of the quantity $\Delta\lambda/\lambda_0$ on temperature. The experimental values, however, all differ by 1.3–1.4, at 200 kv./cm., being larger than those predicted by the Onsager–Wilson theory. This fact is attributed to the presence of magnesium sulfate ion pairs[7] which contribute a Wien effect characteristic of a weak electrolyte, raise the value of the high field conductance, but do not alter the general shape of the high field conductance curve usually observed for strong electrolytes.

While the reproducibility of results on repeated determinations of high field conductance at the same field on individual solutions is 0.03 or better in the term $\Delta\lambda/\lambda_0$ when expressed as per cent., or, in other words, the precision is 0.03%, absolute; the accuracy of the measurements is probably no better than 0.1%, absolute. This is in part ascribed to the comparatively high cell resistances which are required by the 500-ohm output impedance of the pulse power supply. Under such circumstances, the solvent conductance is an appreciable fraction of the cell conductance, approximately 0.6%. In itself this is not a drawback, but since

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(7) F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4428 (1952).

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

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

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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]

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

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

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

where

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

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 α, the degree of dissociation, is computed at zero field from the relation

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

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.)

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

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

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

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

With these numerical values of κ 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 κ as well

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

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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: Λ_X, the equivalent conductance of the electrolyte at finite concentration and at field X; Λ^0, the equivalent conductance of the electrolyte at infinite dilution; e_j, the charge carried by the j ion (with sign); κ, 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]; η, 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); Λ_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; α, the degree of dissociation of the electrolyte under field X; α_0, the degree of dissociation of the electrolyte under zero field; S_Λ, 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).