the value 0.535527 ± 0.000004, from which the atomic weight of vanadium is found to be 50.947.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

ELECTRICAL CONDUCTANCE OF COBALT SULFATE SOLUTIONS[1]

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This paper records the results of an investigation of the conductances of cobalt sulfate solutions, and is the first of a series dealing with the properties of solutions of cobalt salts.

The conductivities of cobalt sulfate solutions have been determined previously by Jones and Jacobson[2] for concentrations varying between N and $N/1024$ at 0, 10, 25 and 35°. This was part of an investigation of the influence of temperature upon the dissociation of thirty-four electrolytes. For reasons to be discussed later, we felt that it was necessary to repeat the measurements of the conductances of cobalt sulfate solutions.

Materials

Conductivity Water.—The conductivity water was prepared by the usual method of redistilling distilled water with alkaline potassium permanganate and condensing the vapor in a block-tin condenser. The water was kept in a six-liter pyrex flask fitted with a siphon and a soda lime tube. All the water used had a conductivity between 1.2×10^{-6} and 2.0×10^{-6} mhos.

Cobalt Sulfate.—Chloropurpureocobalt chloride $[Co(NH_3)_5Cl]Cl_2$ was prepared by the method of Sørensen[3] and was converted to the carbonate and eventually to the sulfate. The cobalt sulfate was precipitated by means of absolute alcohol, and was then twice recrystallized from conductivity water.

Cobalt Sulfate Solutions.—A solution of cobalt sulfate, approximately 0.5 N, was prepared and this was standardized by an electrolytic determination of its cobalt content. The exact amount of conductivity water needed to make the solution exactly 0.5 N was added from a calibrated buret, and from this stock solution was prepared the 0.2 N by diluting 100 cc. of the 0.5 N to a volume of 250 cc. Similarly the 0.1 N solution was prepared by diluting 100 cc. of the 0.5 N to 500 cc. The third "standard" solution 0.05 N was prepared in a similar manner.

In this way three solutions were prepared from the 0.5 N solution. Also duplicate solutions were made by dilution in different ratio, for example, the 0.1 N from the 0.2 N, etc.

The above method was followed for the preparation of the more dilute solutions. In every case at least 100 cc. of a "standard" solution was used in the dilution.

Experimental Method

The conductivity was measured by the Kohlrausch bridge method using two Washburn cells,[4] Types A and B. A new Leeds and Northrup Stu-

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[1] This paper is an abstract of a part of the doctorate thesis of Alfred J. Berger.

[2] H. C. Jones and C. A. Jacobson, *Am. Chem. J.*, **40**, 355 (1908).

[3] Sørensen, *Z. anorg. Chem.*, **5**, 369 (1894).

[4] Washburn, THIS JOURNAL, **38**, 2449 (1916).

dent's Potentiometer was used as the slide wire, and dial resistances were supplemented when necessary by calibrated plug resistances. Plug resistances were used for only three of our measurements, namely, 0.002 N, 0.001 N and in the determination of cell constant of Cell A. Jones and Josephs[5] show that the error due to use of plug resistances not designed for use with alternating current amounts to -0.012% at 1100 cycles for a resistance of 5000 ohms.

The alternating current was furnished by a Leeds and Northrup microphone hummer which maintained a sufficiently pure sine wave of 1000 cycles.[6] Location of the null point was simplified by use of a one-step audio-amplifier of conventional radio design.[7] The capacity necessary to balance that of Cell A was determined by a large calibrated radio condenser, and this capacity was obtained by means of a 0.00075-microfarad fixed condenser shunted with a conventional thirteen-plate variable condenser. This assured a good minimum in the phones at all times (see Fig. 1).

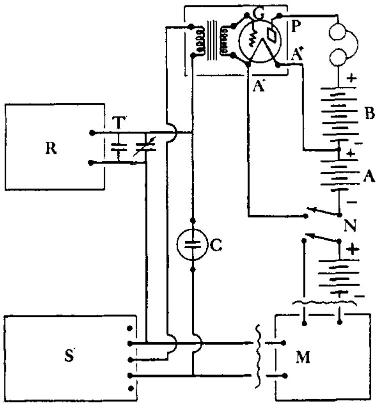

Fig. 1.—Arrangement of apparatus for conductivity measurements. C, Conductivity cell; M, microphone hummer; N, double pole switch; R, resistances; S, student type potentiometer; T, 0.00075 mf.

The cell constant of Cell B was determined with a 0.01 N solution of potassium chloride (twice recrystallized from conductivity water). The potassium chloride solutions were prepared according to the weight method of Kraus and Parker[8] and also according to the volume method of Randall.[9] The cell constants obtained by the use of solutions made by the two methods agreed within 0.05% and the average 0.80373 was taken as the cell constant of Cell B. Bray and Hunt's[10] value for the conductivity of 0.01 N potassium chloride, corrected according to Randall,[11] namely, 0.0014120 mhos, was used in the calculations.

The cell constant of Cell A was obtained by the use of solutions, approximately 0.0005 N, the specific conductivities of which were determined by the use of Cell B, and these values were then used in the calculations of the

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[5] G. Jones and R. C. Josephs, This Journal, **50**, 1081 (1928).

[6] "Experimental Physical Chemistry," by Daniels, Mathews and Williams, McGraw-Hill Book Co. Inc., New York, **1929**, p. 387.

[7] Hall and Adams, This Journal, **41**, 1515 (1919).

[8] Kraus and Parker, *ibid.*, **44**, 2422 (1922).

[9] Randall, *ibid.*, **49**, 1488 (1927).

[10] Bray and Hunt, *ibid.*, **33**, 781 (1911).

[11] Randall and Scalione, *ibid.*, **49**, 1486 (1927).

constant for Cell A.[12] The average value for the cell constant using five different solutions was 0.023206.

Cell B was used between the normalities 0.5 and 0.001 *N*, and Cell A between 0.0005 and 0.0001 *N*. The conductivities of the solutions were measured at 25.00 ± 0.01°.

Results

Table I contains the averages of the specific conductances thus obtained and the equivalent conductances calculated from them. For purposes of comparison the corresponding values for nickel sulfate solutions, as determined by Murata,[13] are also included.

TABLE I

CONDUCTANCE OF COBALT SULFATE SOLUTION AT 25°

Concn., *N*	Specific conductance	Equivalent conductance	$NiSO_4$ (Murata)
1.0	....	.....	29.091
0.5	17718×10^{-6}	35.436	35.222
.2	8778×10^{-6}	43.890	43.585
.1	5111.8×10^{-6}	51.118	50.755
.05	2978.8×10^{-6}	59.576	59.160
.02	1448.2×10^{-6}	72.410	72.254
.01	827.78×10^{-6}	82.778	82.69
.005	466.2×10^{-6}	93.24	93.16
.002	210.0×10^{-6}	105.0	105.49
.001	112.7×10^{-6}	112.7	113.05
.0005	59.35×10^{-6}	118.7	118.66
.0002	24.74×10^{-6}	123.7	124.14
.0001	12.39×10^{-6}	123.9	126.90

Discussion of Results

Ostwald's dilution equation, as deduced from the law of mass action, is as follows: $(C\alpha)^2 = KC(1 - \alpha)$ where $\alpha = \Lambda/\Lambda_0$. Λ is the equivalent conductance of a solution of a given concentration, Λ_0 is the equivalent conductance of a solution of zero concentration. The above equation may be simplified, giving the expression

$$\Lambda = \Lambda_0 - \frac{\Lambda^2 C}{K\Lambda_0} \qquad (1)$$

If we write Equation 1 in the more general form corresponding to Storch's Equation,[14] we get

$$\Lambda = \Lambda_0 - \frac{\Lambda^n C^{n-1}}{K\Lambda_0^{n-1}} \qquad (2)$$

as $\Lambda \longrightarrow \Lambda_0$, this becomes

$$\Lambda \simeq \Lambda_0 - \frac{\Lambda_0 C^{n-1}}{K} \qquad (3)$$

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[12] See Weiland, THIS JOURNAL, **40**, 136 (1918).

[13] Murata, *Bull. Chem. Soc. Japan*, **3**, 47 (1928).

[14] Storch, *Z. physik. Chem.*, **19**, 13 (1896).

Equation 3 suggests the origin of equations of the form

$$\Lambda = \Lambda_0 - BC^{n-1} \qquad (4)$$

Several equations have been proposed of this form. Kohlrausch[15] gives $\Lambda = \Lambda_0 - BC^m$, where $m = {}^1/_3$ or $m = {}^1/_2$. Lorenz[16] and Walden[17] suggest that $m = 0.45$. Debye and Hückel[18] deduce an equation of this form, and show that m should have the value ${}^1/_2$, this value being independent of the nature of the electrolyte.

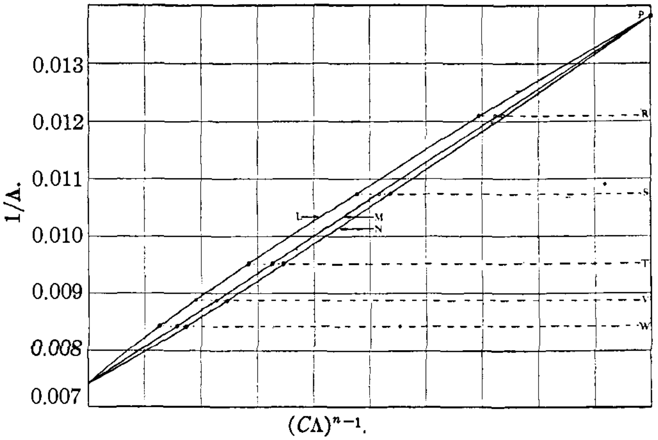
To evaluate n in Equation 2 we have employed the graphic method of A. A. Noyes.[19] Equation 2 is equivalent evidently to

$$\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - \frac{\Lambda^{n-1}\,C^{n-1}}{K\Lambda_0^{n}} \qquad (5)$$

or

$$\frac{1}{\Lambda_0} = \frac{1}{\Lambda} - K'(C\Lambda)^{n-1} \qquad (6)$$

Accordingly, in Fig. 2, the values of $(C\Lambda)^{n-1}$ in the range from 0.0005 to 0.02 N have been plotted as abscissas against the values of $1/\Lambda$ as ordinates, by varying the value of $n - 1$ until a plot as linear as possible was obtained. In this plot we have not included the values for 0.0002 and 0.0001 N, as these are evidently in much greater error than are our other determinations. The value of Λ_0 was obtained graphically by extrapolation of the plotted



L, $n = 1.65$; M, $n = 1.58$; N, $n = 1.55$. P, 0.02 N; R, 0.01 N; S, 0.005 N; T, 0.002 N; V, 0.001 N; W, 0.0005 N.

Fig. 2.—Plot of Storch's function.

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[15] Kohlrausch, "Das Leitvermögen der Elektrolyte," **1916**, p. 107.

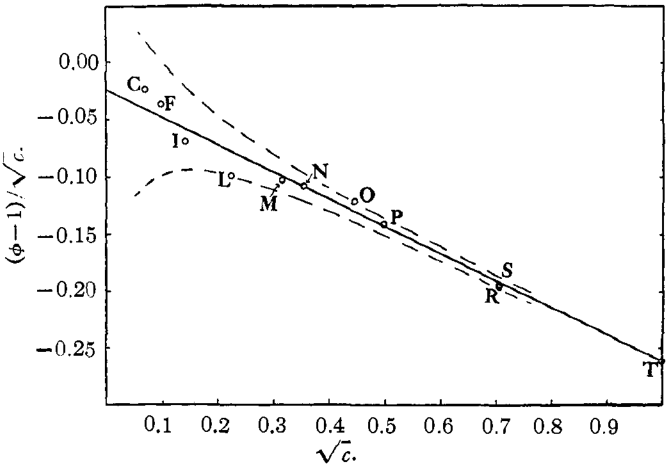
[16] Lorenz, *Z. anorg. Chem.*, **108**, 191 (1919).

[17] Walden, *ibid.*, **115**, 49 (1921).

[18] Debye and Hückel, *Z. Physik*, **24**, 305 (1923).

[19] Noyes and Johnston, This Journal, **31**, 987 (1909); Noyes and Falk, *ibid.*, **34**, 454 (1912).

line to zero concentration where $C\Lambda = 0$. In Fig. 2, in order to make the various curves comparable, the value of $(C\Lambda)^{n-1}$ for the highest concentration (0.02 N) was made 100 for each value of n, and the other values were proportionally varied. The value of the exponent for cobalt sulfate at 25° was found to be 1.58, and the value for Λ_0 was found to be 134.6 mhos at this temperature. It is interesting to note that Murata[13] found the exponent $n = 1.60$, for nickel sulfate at 18 and 25°. According to Noyes and Falk,[19] for all bi-bivalent sulfates n takes a value not far from 1.6 for the concentration interval 0.0001 to 0.02 N. Noyes also points out that the variation of n with the temperature is negligible.



C, 0.005 N; F, 0.01 N; I, 0.2 N; L, 0.5 N; M, 0.1 N; O, 0.2 N; R, 0.5 N. Data of Wagner: N, 0.125 N; P, 0.25 N; S, 0.5 N; T, 1 N. Upper curve, 0.5% deviation; lower curve, 0.5% deviation.

Fig. 3.—Plot of $(\phi - 1)/\sqrt{c}$ for cobalt sulfate at 25°.

We have attempted to apply the Noyes method to Jones and Jacobson's results,[2] that is, we have plotted $1/\Lambda$ against $(C\Lambda)^{n-1}$ for values of $n = 1.58$, $n = 1.50$, $n = 1.40$. The plot for $n = 1.40$ was nearest to a straight line. At $C = 0$, the corresponding $1/\Lambda$ value gave $\Lambda_0 = 154$. However, their points do not fall closely upon a straight line and their final Λ value is 107.05. Hence, such a large extrapolation is not likely to be accurate. Again, the value of n necessary to make the plot approximate a straight line is not in agreement with Noyes' observation that the value for n for most bi-bivalent salts lies close to 1.60.

The Relative Viscosities of Cobalt Sulfate Solutions.—The measurements of relative viscosities were made with an Ostwald viscosimeter in the usual manner. Wagner[20] determined the relative viscosities of cobalt sulfate solutions for concentrations N, $N/2$, $N/4$, $N/8$ at 25°. As a matter

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[20] Wagner, *Z. physik. Chem.*, **5**, 31 (1890).

of interest, we have plotted the Jones and Dole[21] function $(\phi - 1)/\sqrt{c}$ against $\sqrt{c}$ for our values, and have included Wagner's viscosity values on the graph. The resulting curve should be a straight line (see Fig. 3). The maximum deviation of our measurements—for 0.2 N—is 0.56% from that required by the straight line relation. The greatest deviation in Wagner's data—for 0.5 N—is 0.23%. The nature of the plot is such as to magnify the apparent percentage of deviation at the low concentrations.

We have used the viscosity ratio as an *approximate* correction for the mobility term $[(U_{C^+})_0 + (U_{A^-})_0]/U_{C^+} + U_{A^-}$ in the equation[22]

$$\gamma = \frac{\Lambda}{\Lambda_0}\,\frac{(U_{C^+})_0 + (U_{A^-})_0}{U_{C^+} + U_{A^-}}$$

The measurements of the relative viscosities and the conductance–viscosity ratios are given in Table II.

TABLE II

CONDUCTANCE–VISCOSITY RATIOS OF COBALT SULFATE SOLUTIONS

Normality	d^{25}_{25}	$\frac{\Lambda}{\Lambda_0}$	$\frac{\eta}{\eta_0}$	$\frac{\Lambda}{\Lambda_0} \times \frac{\eta}{\eta_0}$
0.5	1.0380	0.26327	1.1613	0.30574
.2	1.0158	.32608	1.0579	.34496
.1	1.0079	.37978	1.0337	.39258
.05	1.0040	.44262	1.0230	.45280
.02	1.0020	.53797	1.0099	.54330
.01	1.0009	.61499	1.0035	.61714
.005	1.0004	.69272	1.0017	.69390
.002	1.0000	.78009	1.0000	.78009
.001	1	.83730	1.0000	.83730
.0005	1	.88187	1	.88187
.0002	1	.91902	1	.91902
.0001	1	.92051	1	.92051

In a later paper we hope to compare these conductance–viscosity ratios with the activity coefficients of the same solutions.

Summary

The conductance of aqueous cobalt sulfate solutions at concentrations 0.0001 to 0.5 N has been measured at 25°.

The exponent n in the equation

$$\Lambda = \Lambda_0 - \frac{\Lambda^n C^{n-1}}{K\Lambda_0^{n-1}}$$

was found to be equal to 1.58 for cobalt sulfate, and Λ_0 by extrapolation by means of this equation was found to be 134.6 mhos.

The relative viscosities of the above solutions have been determined and the conductance–viscosity ratios have been calculated.

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[21] Jones and Dole, THIS JOURNAL, **51**, 2950 (1929).

[22] Noyes and Sherrill, "Chemical Principles," Macmillan Co., New York, **1923**, p. 117.