ELECTRICAL CONDUCTANCE OF NICKEL SULPHATE SOLUTION AND IONIC CONDUCTANCE OF NICKEL.

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In the study of the electrode potential of nickel, the results of which will be presented in another paper by the writer, it was necessary to determine the degrees of ionization of its sulphate solutions.

The degree of ionization of a solution is usually expressed by the relation,

$$\alpha = \frac{\lambda}{\lambda_0}\left(\frac{\eta}{\eta_0}\right),$$

where λ is the equivalent conductance of the solution in question, λ_0 that of an infinitely dilute solution of the electrolyte and η/η_0 is the relative viscosity of the solution which may be taken as unity for sufficiently dilute solutions.

Of these values, the equivalent conductances of nickel sulphate at various concentrations at 25° C. were determined separately by Franke and Jones.⁽¹⁾ However, as these values differ from each other in a not inconsiderable amount, conductivity measurements were made, taking full precaution in preparing the material and in the experiment. Viscosity measurements were also made in parallel.

The equivalent conductance at zero concentration can be calculated by Kohlrausch's principle of additivity from the ionic conductances of the nickel ion and the sulphate ion. Though there are several accurate determinations of the ionic conductance of the latter constituent, Heydweiller's value⁽²⁾ only is known for the ionic conductance of the former. He has derived this value from the values of equivalent conductance at zero concentration of nickel nitrate, chloride and bromide, which were obtained by the Kohlrausch method of plotting the equivalent conductances at various concentrations against the cube-root of the concentrations. But, his values of λ_0 thus obtained are not reliable, because of the too large extrapolation from the points at some high concentrations to that of the infinite dilution and it is therefore desirable to evaluate λ_0 by some other method of greater accuracy. For this purpose, however, the conductance values of nickel salts, given in Kohlrausch and Holborn's table, are not accurate enough and will lead to giving the value of the ionic conductance of nickel a probable error of more than a few percent.

Therefore, the value of λ_0 of nickel sulphate was obtained by Noyes' method⁽³⁾ of using Storch's function from the writer's own values of equivalent conductances at various concentrations, which were determined with sufficient accuracy.

Materials. *Conductivity Water.*—The conductivity water was prepared by the usual method of redistilling ordinary distilled water with alkaline permanganate and condensing it by means of a tin condenser. All the water used had a conductivity between 0.7×10^{-6} and 1.0×10^{-6} reciprocal ohm.

Nickel Sulphate Solutions.—Kahlbaum's cobalt-free nickel sulphate was purified by twice recrystallizations from conductivity water. The separate solutions of nickel sulphate were made up by diluting three standardized stock solutions, 1 N, 0.1 N, and 0.02 N, with the conductivity water to the

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(1) Kohlrausch and Holborn, "Das Leitvermögen der Electrolyte."

(2) *Z. physik. Chem.*, 89 (1915), 281.

(3) Noyes and Falk, *J. Am. Chem. Soc.*, 34 (1912), 462.

accurate normality desired at 25° C. or 18° C.. The standardization of these stock solutions was made by an electroanalysis for nickel using a rotating anode.⁽¹⁾

Measurements of Specific Conductances. *Apparatus and Procedure.*—The conductivity was measured by the ordinary Kohlrausch bridge method, using two cells of the Washburn type A and B.⁽²⁾

The assembly for the measurement consisted of a Kohlrausch bridge with extension coils, a 5-dial Curtis-coil resistance box (both furnished by the Leeds and Northrup Company), Noguchi's special transformer producing a very audible alternating current suitable for the Kohlrausch bridge,⁽³⁾ and a tunable telephone. The slide-wire and the resistance box were calibrated just before the conductivity work was began. The cell constants of the conductivity cells were first determined with a 1/10 normal solution of Kahlbaum's best potassium chloride, and were found to have the values of 1.6856 and 0.1754, respectively. Then these cell constants were checked by means of a 1/50 normal solution of potassium chloride.

The specific conductivities of the solutions were measured at 25°±0.02°C. and at 18°±0.02°C. Immediately after the preparation of each solution its conductivity was measured. After filling the conductivity cell, it was placed in the thermostat and left there for about half an hour. The conductance was then measured twice at an interval of fifteen minutes, in order to be assured that the solution had attained the temperature of the bath. Three separate readings with different resistances gave the conductances, which agree within 0.04 %. The cell was then emptied and refilled with the same solution and confirmative measurement was made. The various determinations of the conductance of the same solution using the same resistance agree within less than 0.02 %.

Results.—Table 1 contains the averages of the specific conductances thus obtained at 25° C. and the equivalent conductances calculated from them and Table 2, those at 18° C.

In both tables, the first column gives the concentration in equivalent per liter at the temperature of the measurement; the second, the cell constant; the third, the measured specific conductance in reciprocal ohms, after the correction for instrumental errors (in the slide wire and the resistance coils); and the fourth, the true specific conductance after the water correction, obtained by subtracting the conductance of water from the value of observed specific conductance in the third column. The mean value of the specific conductances of water was 1.02×10^{-6} at 25° C. and

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(1) Treadwell-Hall, "Analytical Chemistry" II, p. 136.

(2) *J. Am. Chem. Soc.*, 38 (1916), 2449.

(3) *J. of Inst. of Electrical Engineers of Japan*, (1921) 394; (1923), 421.

0.81×10^{-6} at 18° C. in reciprocal ohm. The last column gives the equivalent conductance calculated from the value of the corrected specific conductance in the fourth column.

TABLE 1.

Conductance of Aqueous Nickel Sulphate Solution at 25° C.

Concentration at 25° C.	Cell constant.	Specific conductance.		Equivalent conductance.
		Observed.	Corrected.	
1	1.6856	29091 $\times 10^{-6}$	29091 $\times 10^{-6}$	29.091
0.5	„	17611 „	17611 „	35.222
0.2	„	8717 „	8717 „	43.585
0.1	„	5075.5 „	5075.5 „	50.755
0.05	„	2958.0 „	2958.0 „	59.160
0.02	0.1754	1446.1 „	1445.1 „	72.254
0.01	„	827.9 „	826.9 „	82.69
0.005	„	466.82 „	465.8 „	93.16
0.002	„	212.00 „	210.98 „	105.49
0.001	„	114.07 „	113.05 „	113.05
0.0005	„	60.35 „	59.331 „	118.66
0.0002	„	25.85 „	24.827 „	124.14
0.0001	„	13.71 „	12.690 „	126.90

TABLE 2.

Conductance of Aqueous Nickel Sulphate Solution at 18° C.

Concentration at 18° C.	Cell constant.	Specific conductance.		Equivalent conductance.
		Observed.	Corrected.	
1	1.6856	25066 $\times 10^{-6}$	25066 $\times 10^{-6}$	25.066
0.5	„	15185 „	15185 „	30.370
0.2	„	7519 „	7519 „	37.595
0.1	„	4383.3 „	4383.3 „	43.833
0.05	„	2550.4 „	2550.4 „	51.008
0.02	0.1754	1241.2 „	1240.4 „	62.02
0.01	„	709.7 „	708.9 „	70.89
0.005	„	398.2 „	397.4 „	79.48
0.002	„	180.68 „	179.87 „	89.94
0.001	„	97.12 „	96.31 „	96.31
0.0005	„	51.31 „	50.50 „	101.00
0.0002	„	21.884 „	21.074 „	105.37
0.0001	„	11.680 „	10.870 „	108.70

Calculation of Equivalent Conductance of Nickel Sulphate at Infinite Dilution and Ionic Conductance of Nickel. The value of λ_0 of nickel sulphate was obtained by employing the graphic method of A.A. Noyes.(1)

The method is as follows: Storch's function $C(\lambda_0 - \lambda) = k(C\lambda)^n$, which is equivalent to $\frac{C\alpha}{C(1-\alpha)} = k$, if $\frac{\lambda}{\lambda_0}$ may be taken as a measure of the ionization (α), is transformed into $\frac{1}{\lambda_0} = \frac{1}{\lambda} - k(C\lambda)^{n-1}$, and the values of $(C\lambda)^{n-1}$ in the range from 0.0001 to 0.02 normal are plotted as abscissas against the values of $\frac{1}{\lambda}$ as ordinates, by varying the values of $(n-1)$, until a plot as linear as possible is obtained. The value of λ_0 is obtained graphically by the extrapolation of the plotted line to zero concentration or $C\lambda = 0$. In Fig. 1, in order to make the various curves comparable, the value $(C\lambda)^{n-1}$ for the highest concentration (0.02 normal) was made 100 for each value of n and the other values were proportionally varied by multiplying by the appropriate factors.

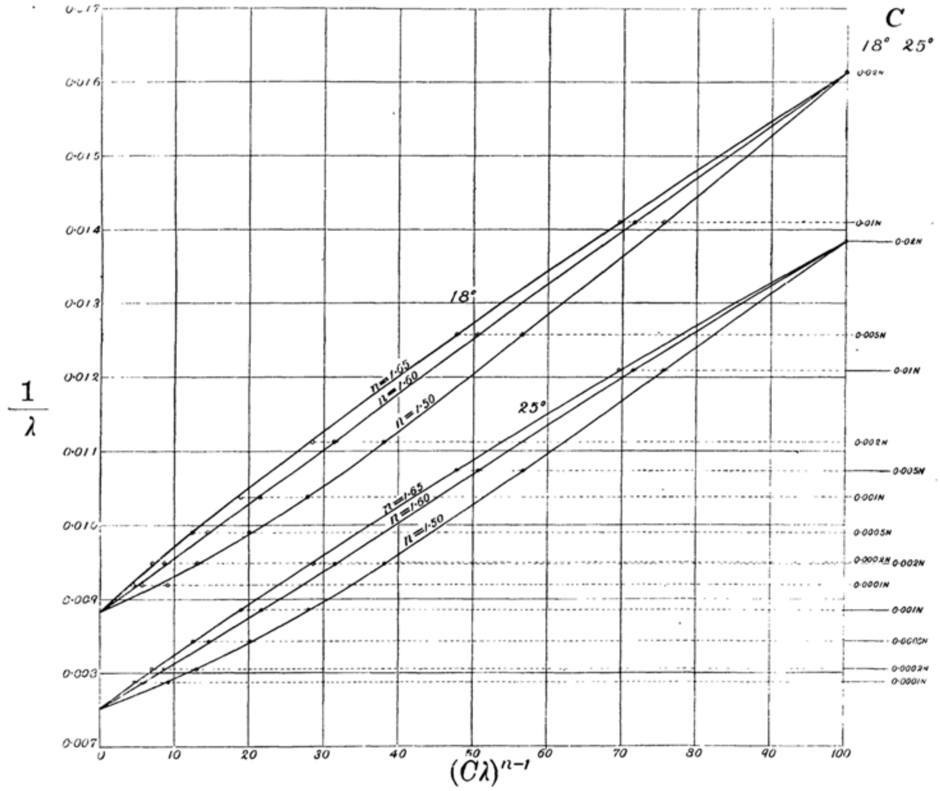

Fig. 1.

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(1) Noyes and Johnston, *J. Am. Chem. Soc.*, **31** (1909), 987; Noyes and Falk, ibid. **34** (1912), 454.

It will be seen from Fig. 1, that the values of the exponent at 25° C. and 18° C. for nickel sulphate were found to be 1.6 in each case for the concentration interval from 0.0001 to 0.02 normal.

It has been found by Noyes and his co-workers that lines nearly straight were obtained with almost the same values of n for the salts of similar type, and according to Noyes and Falk (loc. cit.) for all bi-bivalent sulphates n takes a value not far from 1.6 for the concentration interval from 0.0001 to 0.02 normal. Noyes also pointed out that the variation of the exponent with the temperature is insignificant. Similar results were obtained in the case of nickel sulphate.

Table 3 contains the λ_0 values and the ionic conductances of nickel ion ($\lambda_{\frac{1}{2}Ni}$) computed therefrom and Heydweiller's values are also inserted for comparison.

TABLE 3.

Temperature.	Author.			(Heydweiller.) $\lambda_{\frac{1}{2}Ni^{++}}$
	λ_0	$\lambda_{\frac{1}{2}Ni^{++}}$ (I)	$\lambda_{\frac{1}{2}Ni^{++}}$ (II)	
18° C.	113.6	45.1	45.6	44.
25° C.	133.0	53.0	54.2	52.1

As the value of the ionic conductance of nickel changes in accordance with the value that is taken for the ionic conductance of the sulphate ion, in the calculation of the value in column (I), the necessary datum of $\lambda_{\frac{1}{2}SO_4}$ was obtained from Noyes and Falk's table (loc. cit.) and for column (II), the value of $\lambda_{\frac{1}{2}SO_4}$ in Kohlrausch-Holborn's table was used.

The Relative Viscosity and Degree of Ionization of 1/20 M. Nickel Sulphate. The measurements of relative viscosity were made with Ostwald's viscosimeter and the relative viscosity of 0.05 molal nickel sulphate at 18° C., and 25° C. was found to be 1.0209 and 1.0175, respectively.

The degrees of ionization at this concentration are obtained by using the above corresponding values of λ, λ_0 and η/η_0 at each temperature, thus:

$$\alpha \text{ at } 18^\circ \text{C.} = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{43.833 \times 1.0209}{113.6} = 0.3883$$

$$\alpha \text{ at } 25^\circ \text{C.} = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{50.75 \times 1.0175}{133.0} = 0.3939$$

Summary.

1. The conductances of aqueous solutions of nickel sulphate at concentrations 0.0001 to 1 equivalent per liter at 25° C. and 18° C. were measured and the equivalent conductances at infinite dilution were found.
2. The ionic conductances of nickel also were calculated.
3. The relative viscosity and the degree of ionization of 1/20 mol nickel sulphate were calculated.

In conclusion, the writer wishes to express his thanks to Professor G. Fuseya for his kind direction.

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