Proceedings of the Iowa Academy of Science

1914

The Electrical Conductivity of Solutions of Certain Electrolytes in Organic Solvents

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Recommended Citation

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF CERTAIN ELECTROLYTES IN ORGANIC SOLVENTS.

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The study of the electric conductivity of solutions in organic solvents has brought to light many interesting relations. In many such solvents the same general relation obtains as is found in the case of aqueous solutions, viz., the molecular conductivity increases regularly with increasing dilution. In the great majority of these no limiting value of the molecular conductivity is obtainable, however great the dilution employed.

On the other hand, a large number of instances have been found in which the behavior is apparently just the opposite, the molecular conductivity in these cases increasing as the concentration increases. Instances of this kind are to be observed in the molecular conductivity of solutions of hydrogen chloride in benzene[1], xylene, hexane, and ether; the alkaline halides in benzonitrile[2]; mercuric cyanide in liquid ammonia[3]; aluminium bromide in ethyl bromide[4]; in all the more concentrated solutions of methyl-, ethyl-, n-propyl-, amyl-, and allyl alcohols; phenol, carvacrol, thymol, α- and β-naphthol and resorcinol in liquid hydrogen bromide[5]; various aliphatic and aromatic acids in liquid hydrogen bromide and hydrogen chloride[6]; solutions of the ammonium bases and non-salt organic compounds in the liquid halogen halides and hydrogen sulphide[7]; and solutions of various salts in aniline, methyl aniline, and di-methyl-aniline[8].

Instances are also known in which the molecular conductivity may both increase and then decrease as we proceed from the more dilute to the more concentrated solutions, as for example, solutions of silver nitrate and cadmium iodide in amylamine[9]. Such cases, the authors state, are not to be explained on the basis of the Arrhenius theory. The molecular conductivity of potassium iodide in liquid iodine[10] at first increases with dilution, passes through a maximum and then decreases rapidly.

[1]Kablukoff: Z. physik. Chem., 4, 429; Cattaneo, Real. Accad. Lincei, 1893, ii, 112.
[2]Euler: Z. physik. Chem., 28, 619, 1899.
[3]Franklin and Kraus: Amer. Chem. Journal, 23, 277, 1900.
[4]Plotnikoff: J. Russ. Phys. Chem. Soc., 34, 466, 1902.
[5]Archibald: J. Amer. Chem. Soc., 29, 665, 1907.
[6]Ibid., 29, 1416, 1907.
[7]Steele, McIntosh and Archibald: Z. physik. Chem. 55, 179, 1907.
[8]Sachanov: J. Russ. Phys. Chem. Soc., 42, 683, 1910.
[9]Kahlenberg and Ruhoff: J. Physical Chem., 7, 254, 1903.
[10]Lewis: Proc. Acad. Arts and Sci., 41, 419.

The molecular conductivity of solutions of silver nitrate in methyl-amine[11] first increases with dilution, then decreases and afterward again increases with further dilution. Solutions of lithium chloride in ethylamine[12] give molecular conductivities which increase with dilution up to about 0.8 N and then diminish rapidly with further dilution, while the molecular conductivities of solutions of silver nitrate and ammonium chloride in the same solvent decrease with dilution throughout and finally appear to attain minimum values in the very dilute solutions. Cadmium iodide[13] in certain organic solvents was found to be strikingly abnormal in that its molecular conductivity varies neither with the dilution nor with the temperature.

Many theories have been advanced to explain this apparently abnormal effect of dilution upon the molecular conductivity. Euler[14] explains the increase in the molecular conductivity of solutions in benzonitrile as being due to the presence of the ions. Franklin and Gibbs[15] explain the abnormal results for solutions of silver nitrate in methylamine by means of a slightly modified form of the hypothesis proposed by Lewis[16] for solutions of potassium iodide in liquid iodine. Their hypothesis and explanation is this: ''Salts dissolved in a weak ionizing solvent may be expected to give solutions in which the self-ionization of the salt shows itself conspicuously. Methylamine dissolves silver nitrate abundantly, forming solutions, which, when very concentrated, are possessed of a high degree of viscosity. The conductivity of the most concentrated solutions, in that they approach the condition of the melted salt, is therefore, for the most part, due to the autoionization of the salt. As the solution is diluted its viscosity diminishes rapidly with the result that the increasing speed of the ions more than counteracts the effect of diminishing autoionization, which may be assumed to accompany dilution, and which of itself would cause a diminution of the conductivity. The observed conductivity therefore increases. The viscosity, however, falls off at a rapidly diminishing rate as the dilution increases, so that after a time the opposing effects of viscosity and selfionization balance each other, when a maximum of the molecular conductivity is reached. From this point on, for a time, increasing dilution is most conspicuous in its effects on the autoionization of the salt. The rate at which the autoionization diminishes becomes smaller as the dilution continues to increase with the result that, beyond a certain point, the dissociating action of the solvent becomes conspicuous as the curve passes through

[11]Franklin and Gibbs: J. Amer. Chem. Soc., 29, 1389, 1907.
[12]Shinn: J. Physical Chem., 11, 537, 1907.
[13]Dutoit and Friderich: Bull. Soc. Chim., 1898, iii, 321.
[14]loc. cit.
[15]loc. cit.
[16]loc. cit.

the minimum and then ascends after the familiar manner of salts in aqueous solution.''

Cady[17] noted the similarity between the crystalline compounds of water and copper sulphate on the one hand and ammonia and copper sulphate on the other. Experiments proved that the latter pair also give conducting solutions. It might be inferred from this that whenever a solute and solvent are capable of separating from a solution as a crystalline ''solvate'' solutions of the two components will conduct electricity.

Kahlenberg and Schlundt[18] ventured the idea that the conducting power of a solution is dependent upon a mutual reaction between the solvent and solute resulting in the formation of a compound which conducts the current. This solvent-solute compound theory was further apparently confirmed by Walden and Centnerszwer[19] in their work with solutions in liquid sulphur dioxide. Solutions of lithium chloride in pyridine have remarkably low molecular conductivities. Laszczynski and Gorski[20] explain this as due to the formation of the compound, $LiCl.2C_5H_5N$. That such a theory is useful is very evident, since it can be used in explaining phenomena which are of an opposite nature.

According to Steele, McIntosh and Archibald[21] the power to form conducting solutions is a function of both the solvent and the solute. This belief was strengthened by the fact that amines, alcohols, ether, acetone, etc., which give conducting solutions in the liquid hydrogen halides and hydrogen sulphide, all have the power of forming compounds with these solvents. In their paper they state that it is their object to show that the anomalous behavior of these solutions can be explained upon the basis of the Arrhenius theory, if we assume that the original dissolved substance, of itself incapable of dissociation, may either become polymerized or unite with the solvent to form a compound which can then behave as an electrolyte. For both assumptions, viz., that of polymerization of the solute, or the formation of a solvent-solute compound, they arrive at the general relation,

$$\lambda_v = {}^a K^1 = k V^n,$$

where a represents the degree of dissociation, k the specific conductance, V the volume, K^1 a constant, and n the number of molecules of the solute combining with m molecules of the solvent, or the number of simple molecules of the solute combining to form one molecule of the polymerized solute. Their results when calculated according to this formula show an increase in molecular conductivity with increasing

[17]J. Physical Chem., *1*, 707, 1897.
[18]Ibid., *6*, 447, 1903.
[19]Z. Physik. Chem., *42*, 432, 1903.
[20]Z. Elektrochem., *4*, 290. 1897.
[21]Z. Physik. Chem., *55*, 179, 1907.

dilution, whereas when calculated according to the relation $\lambda_v = kV$, the molecular conductivity decreases with dilution.

Similar results were obtained by Archibald[22] alone for solutions of paraffin and aromatic alcohols in liquid hydrogen bromide and for organic acids in liquid hydrogen bromide and hydrogen chloride.

Sachanov [23] has made an extended study of the conductivity of solutions in some organic solvents. The solvents used were aniline, methylaniline, dimethylaniline, acetic and propionic acids and a few esters. In all of these solvents, except the esters, the molecular conductivity of the various salts used decreases very rapidly with dilution, and this phenomenon is especially marked in the more concentrated solutions. Walden had previously shown that the dissociating power of solvents is in a high degree independent of their chemical nature and is determined chiefly by the dielectric constant of the solvent. The dielectric constants of the solvents used by Sachanov are small. Those of the amines, viz., aniline, methylaniline and dimethylaniline, are 4.79, 6.62 and 4.99, respectively. According to him, the chief factor determining the ability to give conducting solutions is the chemical nature of the solvent. He divides solvents in which diminution of the molecular conductivity is observed into two classes: (1) those in which all solutes, independently of their nature, exhibit such diminution, and (2) those few in which the molecular conductivity, as a rule, increases with dilution, but with certain dissolved substances diminishes. In general, solvents with low dielectric constants are characterized by divergence from the Nernst-Thomson rule. He also states that the decrease of molecular conductivity on dilution is as characteristic a property of solvents with low dielectric constants and slight dissociating power as is the increase of molecular conductivity for solvents with high dielectric constants. The electrolytic dissociation does not depend solely upon the magnitude of the dielectric constant, but also upon the formation of solvates and complex ions, e. g.,

$$Li_2Br_2.xC_6H_7N = \overset{+}{Li.y}C_6H_7N + \overset{-}{LiBr_2}.zC_6H_7N.$$

The formation of such ions favors electrolytic dissociation because the electroaffinity of these ions is greater than that of the primary ions. In solvents with low dielectric constants only complexes which yield ions of greatly enhanced electroaffinity can undergo electrolytic dissociation. The decomposition of these complex solvates and complex ions explains the decrease of molecular conductivity on dilution and also, so he states, why the Nernst-Thomson rule is not applicable for solvents with low dielectric constants.

[22]J. Amer. Chem. Soc., 29, 665, 1416, 1907.
[23]J. Russ. Phys. Chem. Soc., 42, 683, 1363, 1910; 43, 526, 534, 1911; 44, 324, 1912.
Z. Physik. Chem. 80, 13, 20, 1912.

In his study of the dielectric constants of dissolved salts Walden[24] finds that the dielectric constant of a feebly ionizing solvent is increased by dissolving in it certain binary electrolytes and that this increase is apparently dependent upon the constitution of the dissolved salt. On the basis of their specific influence he divides the binary salts chosen into two classes, viz., the strong and the weak. Strong salts, e. g., the tetra-alkylated ammonium salts, which are characterized by a great dissociation tendency, possess also a very high dielectric constant. For weak salts, e. g., the monoalkylated ammonium salts, the reverse is true. They have a slight tendency to dissociate and small dielectric constants. The degree of ionization of a salt depends both on the ionizing power of the solvent and the tendency of the solute to ionize. Since both factors increase with the dielectric constant, the highest degree of ionization will be found in a system where both the solvent and the solute possess large dielectric constants. The presence of free ions was also found to increase the dielectric constant.

A large number of the solutes cited in the introduction, if not all of them, exhibit a strong tendency to polymerize and this tendency obviously increases with the concentration. Depolymerization resulting from dilution may proceed either in separate steps, or directly down to the simplest products. According to Walden, the minimum degradation of the polymeric molecules will be obtained when we dissolve a binary salt with low dielectric constant in a solvent, also with low dielectric constant. In this case the solution will contain an extremely small number of ions, but a very large number of associated salt molecules. The increase in the dielectric constant must therefore be due to the presence of polymerized molecules. These solutions show a weak molecular conductivity. With progressive dilution the dielectric constant falls rapidly and approaches that of the pure solvent. This will result in a rapid decrease in the ionizing power of the solvent and therewith a simultaneous decrease in the molecular conductivity.

It is a well known fact that for a given temperature the complexity of hydrates and of solvates, whether molecules or ions, decreases rapidly with increasing concentration. Furthermore, it has been found that the complexity of these solvates decreases with rise in temperature. On the other hand, the complexity of the solute molecules and ions, due to polymerization, increases with increase in concentration. The effect of temperature would therefore appear in the temperature coefficients of the molecular conductivity.

[24]Bull. Acad. Sci. St. Petersburg. 1912, 305-332, 1055-1086. Translated by H. C. B. Weber, J. Amer. Chem. Soc., 35, 1649, 1913.

The present work was undertaken with the idea of making a detailed study of the molecular conductivity of solutions of electrolytes in various organic solvents over the widest possible range of concentration and to determine the effect of temperature upon the molecular conductivity. This seemed advisable since the previous investigators have limited their work to one temperature.

EXPERIMENTAL.

The conductivity measurements were made by means of the well known Kohlrausch method. The bridge wire was carefully calibrated according to the method of Strouhal and Barus. During the latter part of the work we were fortunate in securing a new Kohlrausch roller bridge of the type devised by Washburn. All of the measuring flasks, burettes, weights and resistance boxes bore the certificate and stamp of the Bureau of Standards, or of the Reichsanstalt. Four glass-stoppered conductivity cells with sealed-in electrodes were used.

The two cells of large resistance capacity were standardized against a 0.02 N potassium chloride solution at 25°C. This solution was prepared from twice recrystalized Kahlbaum's "C.P.", potassium chloride and conductivity water, having a specific conductance of 1.2×10^{-6}, and the specific conductance of the solution was taken as 2.768×10^{-3}. With the cell constants thus obtained the molecular conductivity of a 0.002 N potassium chloride solution was obtained at 25°C. The value of λ_{500} found was: Cell *2=147.64; cell *3=147.60. The constants of the two cells of small capacity were then determined against the 0.002 N solution, and the constants of all four cells checked against a 0.01 N acetic acid solution at 25°.

The temperatures chosen for the work were 0°, 25°, and 35° or 50°C. The zero-bath consisted of clean, finely crushed ice, moistened with distilled water. Large water thermostats, electrically heated and electrically controlled, gave temperatures constant to 25°±.01, 35°±.02 and 50°±.02, respectively.

An attempt was made to use only those salts which are very soluble in the solvent used, in order to get the greatest possible range in concentration, but unfortunately the number of typical salts are few. The salts used were either Kahlbaum's C. P. (best grade), or they were specially prepared. In every case they were carefully purified and dehydrated by the methods recommended for the individual salts and preserved in glass-stoppered weighing bottles over phosphorus pentoxide. The solubility of each salt at 25° was approximately determined and a convenient maximum normality chosen. Whenever possible, the mother solution was made up by direct weighing and then diluted to the con-

centrations desired, the utmost care being taken to prevent contact with the moisture of the air.

SOLUTIONS IN ANILINE.

The aniline used was of an especially good grade from Merck. It had been allowed to stand over fused potassium hydroxide for several weeks. It was then decanted into a clean dry distilling flask and distilled; only the middle portion passing over at 181°-182°C. (uncorr.) was collected. This portion was then further purified according to the method of Hantzsch. The aniline was refluxed for ten hours with a quantity of pure anhydrous acetone, the acetone was distilled off and the middle portion collected. It was finally twice redistilled from pure, powdered zinc. When first distilled the aniline was practically colorless; its specific conductances at 0°, 25° and 35° were $.9 \times 10^{-8}$, 2.4×10^{-8} and 8.2×10^{-8}, respectively. In spite of all precautions taken in its purification, the aniline gradually darkened on standing, but no noticeable change in the specific conductance was to be observed.

Owing to the extremely high resistances it was found impossible to work satisfactorily with solutions more dilute than 0.005 N, while in some cases 0.01 N is the highest dilution measurable.

SILVER NITRATE

TABLE I.—MOLECULAR CONDUCTIVITY.

V.	$\lambda 0^0$	$\lambda 25^0$	$\lambda 35^0$
200	.182	.372	----
100	.159	.349	.423
40	.156	.338	.414
20	.194	.407	.494
10	.299	.650	.738
4	.464	.869	1.418
2	.725	1.984	2.600

TABLE II.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25} - \lambda_0}{\lambda_0 . \ 25}$	$\dfrac{\lambda_{35} - \lambda_0}{\lambda_0 . \ 35}$	$\dfrac{\lambda_{35} - \lambda_{25}}{\lambda_{25} . \ 10}$
100	.049	.048	.021
40	.047	.047	.022
20	.044	.044	.021
10	.047	.046	.021
4	.055	.057	.026
2	.069	.078	.031

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ANILINE HYDROBROMIDE.

TABLE III.—MOLECULAR CONDUCTIVITY.

V.	$\lambda 0^\circ$	$\lambda 25^\circ$	$\lambda 35^\circ$
200	.159	.306	.311
100	.124	.213	.230
40	.109	.183	.185
20	123	.199	.199
10	.170	.263	.264
4	.361	.556	.564
2	----*	.971	1.009

TABLE IV.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda 25^\circ - \lambda 0^\circ}{\lambda_0.\ 25}$	$\dfrac{\lambda_{35} - \lambda_0}{\lambda_0.\ 35}$	$\dfrac{\lambda_{35} - \lambda_{25}}{\lambda_{25}.\ 10}$
200	.037	.027	.001
100	.029	.025	.008
40	.027	.019	.008
20	.025	.017	.000
10	.022	.016	.000
4	.022	.016	.001
2	----*	----*	.003

ANILINE HYDROCHLORIDE.

TABLE V.—MOLECULAR CONDUCTIVITY.

V.	$\lambda 0^\circ$	$\lambda 25^\circ$	$\lambda 35^\circ$
40	.051	.085	.098
20	.048	.079	.088
10	.056	.087	.095
4	.095	.143	.154
2	----*	.265	.286

TABLE VI.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25} - \lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{35} - \lambda_0}{\lambda_0.\ 35}$	$\dfrac{\lambda_{35} - \lambda_{25}}{\lambda_{25}.\ 10}$
40	.026	.025	.014
20	.025	.024	.012
10	.021	.019	.009
4	.020	.017	.007
2	----*	----*	.008

*Solidified.

MONO-ETHYL-ANILINE HYDROCHLORIDE.

TABLE VII.—MOLECULAR CONDUCTIVITY.

V.	$\lambda 0°$	$\lambda 25°$	$\lambda 35°$
100	.064	.112	.119
40	.048	.092	.102
20	.021	.079	.093
10	.053	.084	.089
4	.083	.125	.134

TABLE VIII.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\dfrac{\lambda_{35}-\lambda_0}{\lambda_0 \cdot 35}$	$\dfrac{\lambda_{35}-\lambda_{25}}{\lambda_{25} \cdot 10}$
100	.030	.024	.006
40	.037	.032	.011
20	.109	.097	.018
10	.023	.020	.007
4	.020	.018	.007

MERCURIC IODIDE.

TABLE IX.—MOLECULAR CONDUCTIVITY.

V	λ_0	λ_{25}	λ_{35}
10	.0033	.0076	.0097
2	.0014	.0036	.0046
1	.0012	.0032	.0046

TABLE X.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\dfrac{\lambda_{35}-\lambda_0}{\lambda_0 \cdot 35}$	$\dfrac{\lambda_{35}-\lambda_{25}}{\lambda_{25} \cdot 10}$
10	.053	.053	.027
2	.063	.066	.025
1	.069	.084	.043

AMMONIUM SULPHOCYANIDE.

TABLE XI.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{85}
100	.187	.2588	.312
40	.130	.251	.2919
20	.1647	.313	.3669
10	.267	.506	.8063
4	.647	1.271	1.502

TETRAETHYLAMMONIUM IODIDE.

TABLE XII.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0. \ 25}$
200	.910	2.021	.0488
100	.850	1.910	.0498
40	.964	2.195	.0510
20	1.234	2.842	.0521
10	1.689	3.943	.0534
4	2.244	5.631	.0603
2	2.650	6.849	.0633
1	1.801	5.445	.0809
0.8	1.334	4.477	.0942

SUMMARY OF THE RESULTS IN ANILINE SOLUTIONS.

As might be expected from the nature of the solvent, all of the salts used give poor conducting solutions. In respect to the molecular conductivity these salts may be divided into three classes. In the first class, which includes by far the larger number, are silver nitrate, aniline hydrobromide, aniline hydrochloride, methylaniline-hydrochloride, ammonium sulphocyanide and lithium iodide. With these the molecular conductivity decreases with dilution in the concentrated regions, passes through a minimum and finally increases normally with further dilution. Mercuric iodide, whose molecules usually exhibit a great tendency to polymerize, gives values for the molecular conductivity which apparently increase normally with the dilution. For tetraethyl-ammonium iodide, on the other hand, the molecular conductivity first increases with the dilution to a maximum, then decreases rapidly, passes through a minimum and finally again increases normally with the dilution. The behavior of tetraethylammonium iodide is similar to

that found by Franklin and Gibbs[25] for solutions of silver nitrate in methylamine. Of the salts studied tetraethylammonium iodide gives the best and mercuric iodide the poorest conducting solution.

The effect of temperature varies with the nature of the dissolved salt. The temperature coefficients of the molecular conductivity of solutions of silver nitrate, aniline hydrochloride, and aniline hydrobromide decrease with dilution in the concentrated regions and pass through a minimum in those solutions which give the minimum value for the molecular conductivity. Methylaniline hydrochloride, on the contrary, gives a maximum temperature coefficient in that concentration which gives the minimum molecular conductivity. Although but three concentrations of mercuric iodide were studied, the temperature coefficients show a distinct increase with increasing dilution, while for tetraethyl-ammonium iodide the temperature coefficients decrease throughout with increasing dilution, the decrease being most rapid in the regions of greatest concentration.

SOLUTIONS IN QUINOLINE.[26]

Schuchardt's chemically pure, synthetic quinoline was allowed to stand over fused potassium hydroxide for several weeks and then twice redistilled. Only that portion passing over at 227-229° C. was used in the work. In order to make the effect of the temperature greater, the molecular conductivities were determined at 50°, instead of at 35°, as in the case of aniline. The specific conductivities of the quinoline at 0°, 25° and 50° were found to be 1.6×10^{-8}, 2.2×10^{-8} and 7.4×10^{-8}, respectively.

Rough determinations of the solubility of many salts in quinoline showed that only a very few are sufficiently soluble to make work with them worth while. Of these the three chosen are aniline hydrobromide, silver nitrate and cobalt chloride.

[25]loc. cit.
[26]The work with solutions in quinoline was performed by Mr. E. H. Conroy.

ANILINE HYDROBROMIDE.

TABLE XIII.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
1,000	.596	.918	1.319
500	.480	.760	.988
200	.340	.528	.666
100	.267	.416	.527
20	.207	.324	.412
5	.264	.464	.642

TABLE XIV.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0 \cdot 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25} \cdot 25}$
1,000	.0216	.0243	.0175
500	.0236	.0212	.0151
200	.0221	.0192	.0105
100	.0233	.0195	.0107
20	.0266	.0198	.0109
5	.0303	.0286	.0153

SILVER NITRATE.

TABLE XV.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
1,000	2.327	----	----
500	2.158	3.254	4.101
200	1.951	3.115	4.005
100	1.669	2.574	3.178
20	1.443	2.273	2.842
10	1.397	2.246	2.896
5	1.270	2.275	3.197

TABLE XVI.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0 \cdot 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25} \cdot 25}$
500	.0204	.0180	.0104
200	.0239	.0210	.0114
100	.0217	.0181	.0094
20	.0231	.0194	.0100
10	.0244	.0215	.0116
5	.0317	.0303	.0162

COBALT CHLORIDE.

TABLE XVII.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
266.6	.1042	.1933	.3110
500	.253	.464	.599
1,000	.293	.499	.653

TABLE XVIII.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
266.6	.0342	.0398	.0245
500	.0334	.0274	.0116
1,000	.0281	.0246	.0123

In view of the fact that quinoline has a higher dielectric constant than aniline, we should expect that solutions in it should give higher molecular conductivities. This is found to be true for silver nitrate and aniline hydrobromide. The minimum of molecular conductivity is displaced toward the region of higher concentration and the molecular conductivity increases rapidly with the dilution. The temperature coefficients pass through a minimum, but at dilutions which are greater than those which give the minimum molecular conductivity. Owing to the rather slight solubility of the cobalt chloride, only three concentrations of this salt were studied. In these the molecular conductivity increases with dilution, while the temperature coefficients decrease under the same conditions.

SOLUTIONS IN PYRIDINE.[27]

Merck's best grade of pyridine was allowed to stand over fused potassium hydroxide for several months, then decanted and twice redistilled. Only the middle portion passing over at 115°-116.1° and 745 mm. was retained for the work. Its specific conductances at 0°, 25° and 50° were found to be $.57 \times 10^{-7}$, $.74 \times 10^{-7}$ and 1.2×10^{-7}, respectively. Lincoln[28] found the specific conductance of the pyridine which he used to have the much higher value of 7.6×10^{-7}.

Those salts which do not show hygroscopic properties were weighed directly, transferred to a certified volumetric flask and made up to

[27]The data for the pyridine solutions are taken from a thesis begun by Mr. E. X. Anderson. Since the completion of the thesis appeared doubtful, it was thought advisable to include the data in the present paper.

volume, but for those salts which do absorb moisture the method of weighing by difference was used. The pyridine was added directly to the flask from a specially devised filling apparatus, whose open ends were always protected by phosphorus pentoxide tubes. The dilute solutions were made by diluting the mother solution, the utmost care being taken to prevent contact with the moisture of the air.

SILVER NITRATE.

TABLE XIX.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
1	1.05	1.53	2.01
2	14.77	19.38	23.28
10	20.68	25.38	27.25
20	22.38	27.05	29.17
100	27.80	34.49	37.92
500	37.31	47.63	55.10

TABLE XX.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
1	.0149	.0133	.0121
2	.0125	.0114	.0081
10	.0091	.0064	.0029
20	.0084	.0061	.0031
100	.0096	.0073	.0040
500	.0111	.0095	.0063

The values for λ_{25} here given agree very closely with those given by Lincoln[28] for the same salt at 25°. The molecular conductivity increases at first very rapidly with slight changes in dilution in the concentrated regions and then more slowly at higher dilutions. The temperature coefficients show a very rapid decrease in the concentrated solutions.

It will be seen that the molecular conductivities at first increase very rapidly with slight increase in dilution, and then less rapidly, with further dilution for all three temperatures. The temperature coefficients show distinct minima, the effect of temperature upon the conductivity being greatest in the concentrated solutions.

Although solutions of silver nitrate in pyridine possess a relatively high molecular conductivity, Walden and Centnerszwer[29] have found that the molecular weights of silver nitrate in dilute solutions of pyridine are normal, while in the concentrated solutions the molecular weights are greater than normal, thus indicating association. By the

[28]J. Physical Chem., 3, 457, 1899.
[29]Z. physik. Chem., 55, 321, 1906.

same method Schmujlow[30] found that this salt is apparently non-ionized, but, since transference experiments made by Neustadt and Abegg[31] showed that both the $\overset{+}{Ag}$ ion and the NO_3 radicle migrated toward the cathode, it was assumed that, if ionization does take place, it does so according to the equation,

$$2AgNO_3 = \overset{+}{Ag_2NO_3} + \overset{-}{NO_3}$$
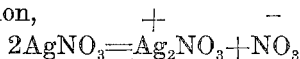
It is obvious that if the amount of polymerization just compensates for the effect due to ionization, the total number of dissolved particles will be the same as they would be if neither polymerization nor ionization had occurred. The molecular weights obtained by the boiling point-method should be normal. As the concentration is increased, on the other hand, polymerization rapidly increases, while the degree of dissociation decreases, a result which is interpreted by some to indicate the presence of polymerization and the absence of ionization. That the simple $\overset{+}{Ag}$ ions are also present even in the concentrated solutions is not to be doubted.

LITHIUM CHLORIDE.

The pure salt was heated at 160° for several days, it was frequently pulverized in a hot agate mortar and the heating continued until the tendency to cake had ceased. It was then transferred to a weighing bottle and heated to constant weight.

TABLE XXI.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
0.58	.143	.199	.239
1.6	.218	.264	.282
2	.254	.290	.299
10	.279	.322	.346
100	.519	.573	.613
1,000	1.47	1.600	1.680

TABLE XXII.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 . \ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0 . \ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25} . \ 25}$
0.586	.0160	.0135	.0079
1	.0083	.0058	.0028
2	.0056	.0035	.0012
10	.0061	.0047	.0030
100	.0041	.0036	.0028
1,000	.0037	.0029	.0020

[30]Z. f. anorgan. Chem., 15, 1897.
[31]Z. Physik. Chem., 69, 436, 1910.

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Lithium chloride is at best a very poor conductor and is but slightly dissociated at all dilutions and temperatures. In other solvents it shows a high tendency to polymerize and doubtless does so in pyridine solutions. The molecular conductivities do increase gradually with increasing dilution throughout the whole range of concentration. The values found by Laszczynski and Gorski[32] for the same solution are about four times larger, due, perhaps, to the presence of traces of moisture. The temperature coefficients decrease with dilution throughout, the greatest changes being in the most concentrated solutions.

LITHIUM BROMIDE.

The anhydrous salt was prepared in a manner similar to that used for lithium chloride.

TABLE XXIII.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
0.977	____*	1.29	1.65
2	.98	1.72	1.98
10	2.29	2.44	2.40
100	5.43	5.34	4.89
1,000	13.68	14.15	13.58
10,000	24.80	28.70	29.9

TABLE XXIV.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0 \cdot 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25} \cdot 25}$
0.97	____	____	.0109
2	.0298	.0202	.0061
10	.0026	.0009	−.0006
100	−.0007	−.0020	−.0034
1,000	.0013	−.0001	−.0016
10,000	.0063	.0041	.0017

*Solidified.

For all temperatures the molecular conductivity increases steadily throughout with increasing dilution, but not at all dilutions with a rise in temperature, there being at certain dilutions a decrease in conductivity with increase in temperature. The temperature coefficients are in all except the most concentrated solutions very small. They pass through minima of negative value.

[32] Z. Elektrochem., 4, 290, 1897.

LITHIUM IODIDE.

This salt, after several months' standing over phosphorus pentoxide, was heated for nearly one week at 150°.

TABLE XXV.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
1	4.40	7.04	9.82
2	7.79	10.98	13.82
10	12.76	16.40	18.62
100	18.34	23.35	25.98
1,000	27.10	35.99	42.65
10,000	31.20	44.4	50.50
inf.	(31.2)*	(44.9)	(50.5)

*Extrapolation.

TABLE XXVI.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
1	.0224	.0246	.0158
2	.0164	.0155	.0103
10	.0114	.0092	.0054
100	.0109	.0083	.0045
1,000	.0131	.0115	.0074
10,000	.0169	.0124	.0055

From Table XXV it will be observed that lithium iodide is a good conductor. The molecular conductivity increases very rapidly for slight dilution in the concentrated regions and then more slowly, but steadily up to a maximum at ten thousand liters. The temperature coefficients pass through a minimum at a dilution of one hundred liters.

SODIUM IODIDE.

TABLE XXVII.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
1.33	.11*	.70	.84
5	10.00	11.14	11.20
10	14.56	16.15	15.80
100	21.66	23.81	22.87
1,000	32.99	39.53	41.28
10,000	42.20	56.70	63.20

TABLE XXVIII.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
1.33	.2084*	.1279*	.0076
5	.0046	.0024	.0002
10	.0044	.0017	−.0009
100	.0040	.0011	−.0016
1,000	.0079	.0050	.0018
10,000	.0137	.0099	.0046

*Solid phase present.

Sodium iodide solutions in pyridine are good conductors at all dilutions, except those near the point of saturation, where the molecular conductivities are very small at all temperatures. By extrapolation λ inf. was found to be 43.3 at 0°. Laszczynski and Gorski[33] obtained 44.32 for the value of λ inf. at 18°. For 25° and 50° no limiting values of the molecular conductivity could be found; at these temperatures the conductivity continues to increase with dilution more rapidly than at 0°. The temperature coefficients exhibit well defined minima with negative values appearing for temperatures between 25° and 50°.

POTASSIUM THIOCYANATE.

The sample was recrystallized from absolute alcohol, washed with the alcohol and dried at 95°. This salt differs from the others that have been studied in that its solubility in pyridine decreases as the temperature rises.

TABLE XXIX.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
7	5.97	7.12	7.75
14	7.20	8.45	9.00
70	11.40	13.36	14.54
140	14.17	16.77	18.14
1,400	27.32	33.70	38.31
14,000	42.86	58.51	71.30
inf.	46.5*	----	----

TABLE XXX.   TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 . 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0 . 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25} . 25}$
7	.0077	.0060	.0035
14	.0069	.0050	.0026
70	.0070	.0055	.0035
140	.0073	.0056	.0033
1,400	.0093	.0081	.0055
14,000	.0146	.0133	.0087

*By extrapolation.

Apparently the conditions which tend to produce a decrease in solubility with rise in temperature are those which have to do with rapid increase in conductivity at higher temperatures. The temperature coefficients here also pass through a minimum.

AMMONIUM THIOCYANATE.

The anhydrous salt was prepared in the same manner as was the potassium salt.

TABLE XXXI.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
.33	2.10	4.46	7.43
1	8.21	11.70	15.12
2	10.45	13.76	16.53
10	11.96	14.56	16.29
100	17.00	20.33	22.18
1,000	33.57	41.80	47.76

TABLE XXXII.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0 \cdot 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25} \cdot 25}$
.33	.0451	.0508	.0266
1	.0170	.0169	.0117
2	.0127	.0116	.0081
10	.0087	.0072	.0048
100	.0078	.0061	.0036
1,000	.0098	.0085	.0057

The molecular conductivity curves for ammonium thiocyanate are peculiar in that they rise rapidly with slight increase in dilution, then rise slowly for a considerable change in dilution, and finally increase rapidly as the dilution is further increased. The values for λ_v are considerably larger than those found by Laszczynski and Gorski. Working up to dilution of 2080 liters, these men calculated the value of λ *inf.* at 18° to be 40.22. In the curves for the above tables it is clearly seen that the 0° curve gives promise of a limiting value for λ_v, but the 25°- and 50°-curves give no signs of such a behavior.

The initial rapid increase in the molecular conductivities and decrease in the temperature coefficients are undoubtedly due to a rapid decrease in the viscosity of the concentrated solutions with slight increase in dilution. The concentrated solutions here used are very viscous.

IOWA ACADEMY OF SCIENCE.

MERCURIC CHLORIDE.

TABLE XXXIII.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
.5	.009*	.036	.045
1	.019	.025	.030
2	.016	.021	.025
10	.016	.021	.027
100	.037	.061	.067
1,000	.130	.260	.400

TABLE XXXIV.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
.5	.1176*	.0793	.0104
1	.0136	.0119	.0076
2	.0126	.0105	.0065
10	.0126	.0141	.0119?
100	.0260	.0162	.0038
1,000	.0400	.0415	.0215

MERCURIC BROMIDE.

TABLE XXXV.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
.5	.012*	.034	.043
1	.020	.026	.032
2	.018	.023	.026
10	.017	.023	.028
100	.031	.047	.053
1,000	.130	.280	.290

MERCURIC IODIDE.

TABLE XXXVI.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
.66	*	.013	.018
1	.009	.013	.018
2	.008	.012	.015
10	.013	.019	.024
100	.069	.102	.117
1,000	.266	.364	.448

*Solid phase present.

The conductivities of the mercuric halide salts are extremely poor. With increase in dilution the molecular conductivity varies but little and only begins to show an appreciable increase at a dilution of one hundred liters. All three of the salts show faint but distinct minima in the molecular conductivity. Since the molecular conductivities are so small, any slight errors in them will be highly magnified in the temperature coefficients. The values of the latter are all of the same order of magnitude as those given for mercuric chloride and all three salts give minima for temperature coefficients.

The value for λ_v for mercuric iodide are much smaller than those obtained by Lincoln[34] at 25°.

COPPER CHLORIDE.

Kahlbaum's C. P. cupric chloride was heated for several hours in a current of pure dry hydrogen chloride at 160°, then heated in a current of dry hydrogen, and cooled in a current of the latter; lastly, it was quickly transferred to a weighing bottle and further heated in an air-bath at 160°.

TABLE XXXVII.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
25	.053	.062	.074
50	.066	.076	.086
100	.088	.098	.111
200	.130	.146	.171
500	.203	.216	.216?
1,000	.302	.365	.410

TABLE XXXVIII.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0 \cdot 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25} \cdot 25}$
25	.0073	.0082	.0076
50	.0059	.0059	.0052
100	.0045	.0053	.0055
200	.0050	.0063	.0068
500	.0027	.0014	.0000
1,000	.0084	.0072	.0049

The molecular conductivities for all temperatures increase steadily with increase in dilution. While more or less irregular, the temperature coefficients exhibit a minimum value in the dilute regions.

[34]loc. cit.

Kohlschuetter[35] states that cupric chloride dissolved in pyridine gives a blue solution, and since its molecular weight, as determined by the boiling point method, is normal, its color may be attributed to that of the undissociated cupric chloride. Naumann[36] has also observed this blue color in his work and assumes it to be due to the presence of the complex, $CuCl_2.2Pyr$. All of the cupric chloride solutions used in this work gave a beautiful, deep green color without the least indication of a bluish tint and, furthermore, the solutions remained green for several months. On the other hand, in making one of the trial solubility tests an attempt was made to weigh the salt directly. The salt absorbed moisture so rapidly that this was impossible. Although it was noticed that the edges of the salt mass had taken on a greenish blue color, it was quickly transferred and dissolved in pyridine and, as might be expected, the solution was perfectly blue. When, however, the salt was quickly weighed by difference, a deep green solution was always obtained. It is evident, therefore, that the blue solutions reported by Kohlschuetter and Naumann owe their blue color to traces of water.

COPPER NITRATE.

A .1N solution of silver nitrate was treated with an excess of finely divided, reduced metallic copper and allowed to stand until the solution gave no test for silver.

TABLE XXXIX.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
10	9.68	12.94	14.96
20	5.00	7.21	8.88
40	8.57	11.60	14.16
100	12.08	16.43	20.43
1,000	16.41	23.88	29.71
10,000	19.42	27.24	35.71

TABLE XL.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
10	.0135	.0109	.0062
20	.0176	.0155	.0093
40	.0142	.0131	.0088
100	.0144	.0138	.0097
1,000	.0158	.0162	.0119
10,000	.0161	.0168	0124

Copper nitrate gives far better conducting solutions than does the chloride.

[35]Ber., 37, 1153, 1904.
[36]Ber., 37, 4609, 1904.

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COBALT CHLORIDE.

The pure salt was first partially dehydrated by long standing over phosphorus pentoxide and then successfully treated according to the method employed for copper chloride. The final product was of a pale blue color. Reitzenstein[37] prepared the compound $CoCl_2.4Pyr$. Pearce and Moore[38] found that within their respective temperature limits we may have the three compounds, $CoCl_2.6Pyr$, $CoCl_2.4Pyr$, and $CoCl_2.2Pyr$.

Cobalt chloride dissolved in pyridine gives a red solution at $0°$, a violet at $25°$, and a deep purple at $50°$. These color changes at different temperature are doubtless closely associated with changes in the amount of pyridine combined with the salt, since the colors of the solid phases in contact with the saturated solutions at these temperatures are aproximately the same as those of the solutions.

TABLE XLI.—MOLECULAR CONDUCTIVITY.

V.	λ_0	λ_{25}	λ_{50}
10	.009*	.012	.021
20	.015	.015	.022
40	.021	.020	.024
100	.042	.045	.041
1,000	.220	.230	.310
10,000	.600	1.00	------

TABLE XLII.—TEMPERATURE COEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_0.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
10	.0148*	.0393	.0319*
20	.0019	.0101	.0174
40	−.0021	.0028	.0082
100	.0028	−.0005	−.0036
1,000	.0018	.0082	.0139

*Solid phase present.

Cobalt chloride in pyridine solutions gives at best exceedingly poor conducting solutions. By some its solutions are considered as non-conductors. Consequently, slight errors are highly magnified. The results obtained show a continuous increase in molecular conductivity with dilution for all temperatures. Lincoln's values for λ_v at corresponding

[37]Ann. Phys. Chem., 43, 839.
[38]Amer. Chem. Jour., 50, 231, 1913.

dilutions are very much higher than the values here given. The temperature coefficients, although subject to error, show definite minima at which negative coefficients are observed. As is evident from table XLII, the effect of temperature is greater between 25° and 50° than at the lower temperatures. This is, no doubt, due to the greater instability of the solvated ions at higher temperatures.

CADMIUM NITRATE.

The solution of the pure salt was prepared by displacing the silver of a .1N solution of silver nitrate by means of pure metallic cadmium.

TABLE XLIII.—MOLECULAR CONDUCTIVITY

V.	λ_0	λ_{25}	λ_{50}
10	.141	.160	.122
20	.322	.348	.288
40	.402	.433	.340
100	.694	.733	.630
1,000	2.370	2.310	2.440
10,000	7.400	8.600	9.800

TABLE XLIV.—TEMPERATURE COEEFFICIENTS.

V.	$\dfrac{\lambda_{25}-\lambda_0}{\lambda_{25}.\ 25}$	$\dfrac{\lambda_{50}-\lambda_0}{\lambda_0.\ 50}$	$\dfrac{\lambda_{50}-\lambda_{25}}{\lambda_{25}.\ 25}$
10	.0052	−.0028	−.0095
20	.0033	−.0021	−.0070
40	.0031	−.0031	−.0086
100	.0023	−.0018	−.0056
1,000	−.0010	.0006	.0023
10,000	.0065	.0065	.0056

Solutions of cadmium nitrate would be classed as poor conductors; the values of λ_v increase with dilution throughout. For the concentrated solutions increase of temperature above 25° produces a rapid decrease in conductivity and, as the temperature coefficients show, this decrease is greater between 25° and 50° than between 0° and 25°. An explanation for this phenomenon will be given in the discussion.

SUMMARY OF THE RESULTS IN PYRIDINE SOLUTIONS.

The molecular conductivities of fourteen salts and their temperature coefficients have been determined in pyridine solutions. These salts may be divided into two classes, the strong and the weak. Among the former

are silver nitrate, lithium iodide, sodium iodide, potassium and ammonium thiocyanates and copper nitrate. The values for λ_v of these salts are very small in the most concentrated solutions, but they increase rapidly with slight initial dilutions and then more slowly with further increase in dilution. All of them give minima in the temperature coefficients, except copper nitrate whose temperature coefficients seem to increase steadily with dilution.

The weak salts are lithium chloride, lithium bromide, the three mercuric halides, copper chloride, cobalt chloride and cadmium nitrate. Only the mercuric salts give minimum values for λ_v; the molecular conductivity of the others increases slowly with increasing dilution. All but one of the salts of this group give minimum values for the temperature coefficients; those of lithium chloride decrease with dilution. Negative temperature coefficients have been found for solutions of sodium iodide, lithium bromide, cobalt chloride and cadmium nitrate.

DISCUSSION.

The molecular conductivity of a solution of an electrolyte is dependent first upon the nature of the solvent and primarily upon its dielectric constant, or specific inductive capacity. According to the Nernst-Thomson rule, the dissociating power of a solvent will be greater, the greater is its dielectric constant.

Walden[39] has found that the dielectric constants of solvents of feeble ionizing power are increased by dissolving in them certain binary salts. The amount of this increase depends upon the constitution of the salt used. According to him salts may be divided into two classes, the strong and the weak. Strong salts exhibit a great tendency to ionize and possess large dielectric constants, while in a weak salt both of these are small. The degree of ionization of a salt depends both on the ionizing power of the solvent and the tendency of the salt to ionize. As both of these factors increase with the dielectric constant, the highest degree of ionization will be found in a system where both the solvent and the solute possess large dielectric constants.

The molecular conductivity also depends upon the degree of dissociation of the electrolyte, the nature of the ions, their speeds and the viscosity of the solutions. The degree of dissociation depends upon the magnitude of the electroaffinities of the ions formed. It will also be more or less affected by the degree of solvation of the molecules and ions present, since, doubtless, the energy of the simple and polymerized

[39]Bull. Accad. Sci. St. Petersburg, 1912, 305-332.

molecules, as well as the electroaffinities of the ions must be somewhat modified by combination with the solvent. If degradation of energy accompanies an increase in electroaffinity, then, as Sachanov[40] states, the electroaffinity of the ions must increase with solvation and, for a given electrolyte, will be greater, the more dilute is the solution.

The speeds of the ions, if they have the power of combining with the solvent, must also be greatly affected by solvation; the greater the amount of solvation, the greater will be their mass, or volume, and, therefore, the smaller will be their migration velocities. Since, according to the Law of Mass Action, the degree of solvation of the ions must increase with increasing dilution, the effect of solvation upon the ionic velocities will be greatest in the most dilute solutions.

The stability of the solvated ions (also molecules) decreases with rise in temperature. If we consider solutions which are dilute with respect to a given ion, we should expect to find the effect of temperature to increase with dilution. That this is true may be seen from a study of the temperature coefficients given in this paper.

According to Noyes and Coolidge[41], the molecular conductivity of aqueous solutions for a given concentration, increases steadily with rise in temperature up to 306°, the increase being due chiefly to a steady decrease in viscosity. The rate of decrease in dissociation of the salt is small between 18° and 100°, but becomes much larger for higher temperatures. This decrease is evidently due to a change in the nature of the solvent, i. e., a decrease in its degree of association and, hence, in its dissociating power.

If the formation of ions depends to any extent upon the power of these ions to combine with the solvent, an increase in temperature should be accompanied by a decrease in ionization and likewise in molecular conductivity. It has been noted that lithium bromide, sodium iodide, cobalt chloride and cadmium nitrate in pyridine give negative temperature coefficients. For lithium bromide the value of λ for a .01 N solution decreases slowly from 0° to 25° and then more rapidly up to 50°, while the same values for the other three salts increase up to 25° and then decrease with rise in temperature. All of these show a tendency not only to form polymeric molecules in pyridine, but also the power to form pyridine-solute complexes. The effect of temperature on these solvates is clearly indicated by the color changes in the cobalt chloride solutions. These salts also have the power to form complex ions which, doubtless, also have a great tendency to form solvates. It will be ob-

[40]loc. cit.
[41]Z. physik. Chem., *46*, 323, 1903.

served also that these negative temperature coefficients are those of minimum value. They are likewise found in those concentrations in which the concentration of the complex ions is least and hence most highly solvated. The effect of temperature upon the unstable solvent-ion complexes will therefore be greatest at this point. If, again, the formation of these ions depends upon their power to combine with the solvent, then the degree of ionization should decrease with rise in temperature. This assumption agrees perfectly with the results obtained.

It was for a time believed that the molecular conductivity of an electrolyte in solution must increase with dilution. Then appeared the above cited work in organic solvents which, in the minds of some chemists, completely overthrew the whole electrolytic dissociation theory. In practically all of these cases the molecular conductivity was found to decrease with increasing dilution. Unfortunately, these investigators seem to have stopped too soon. Had they but continued their work at greater dilutions, they would probably have found that in very dilute solutions in these solvents the molecular conductivity behaves normally as in aqueous solutions.

This has been found to be true for solutions in aniline, quinoline and pyridine, without exception. There are also solutes which in these three solvents show increase in conductivity throughout the whole range of dilution.

The three solvents chosen are but slightly, if at all, associated and they have small dielectric constants, viz., aniline$=7.31$[42], quinoline$=8.8$[43], pyridine$=12.4$[43]. The ionizing power of the solvents and the conductivity of their solutions increase from aniline to pyridine. Salts dissolved in them give, for the most part, low molecular conductivities and exhibit a great tendency not only to polymerize, but also to combine with the solvent. It is probable that there are present at all dilutions to a greater or less extent both the simple and polymeric molecules and their ions, as well as the solvated forms of each.

We may represent the condition of equilibrium existing in a solution by the following scheme:

$$\overset{+}{Li.S_1}+\overset{-}{Br.S_2}=LiBr.S_3=(LiBr)_2.S_4=\overset{+}{Li.S_1}+\overset{-}{LiBr_2.S_5,}$$
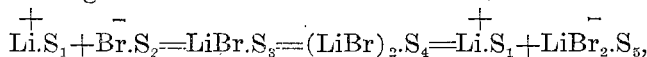
where S_1, S_2, S_3, etc., represent the number of molecules of combined solvent. The two molecular forms are in equilibrium with each other and also with their respective ions.

Unfortunately, we have no means of arriving at any conclusions as to the complexity of the solute in these solvents, except by the boiling-

[42]Turner: Z. Physik. Chem., 35, 385. 1900.
[43]Schlundt: J. Physical Chem., 5, 157, 1901.

point method and this is not applicable in the very dilute solutions. The assertion that simple molecules predominate in the dilute solutions is supported by experiments upon the molecular weights of alcohol, acetic acid and phenol in benzene. The molecular weights are smallest in the dilute regions and increase rapidly with increase in concentration, e. g.,

	Concentration percent.	Mol. Weight found.	Mol. weight Theory.
Alcohol	.161	46	46
	32.50	318	
Phenol	.34	144	94
	26.8	252	
Acetic acid	.465	110	60
	22.8	153	

Most of the salts used in this work show by the boiling-point method either normal molecular weights or slight association. That these solutions contain ions is obvious from the fact that they conduct electricity. It is obvious also that the phenomena of ionization, polymerization and solvation may all exist at the same time and still give normal molecular weights, since the effect due to polymerization of the solute molecules under the conditions need only be just sufficient to counteract the effects due to ionization and solvation.

Returning to our equilibrium equation, it is evident that, if we begin with the most dilute solutions and increase the concentration, there will be a repression of the simple ionization with the formation of simple molecules. The molecular conductivity in the dilute solutions should, and does, decrease with increase in concentration.
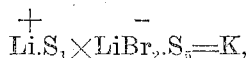
With the increase in concentration of the simple molecules there is an accompanying increase in the number of the more easily ionizing polymerized molecules.

Normally, the molecular conductivity of any salt, whether simple or complex, should decrease with increase in concentration, whereas in many solvents the reverse is true. One way of explaining this phenomenon seems to have been overlooked, one which at least seems logical and in harmony with the facts.

Let us take a solution of a salt at a dilution which is far beyond that dilution which just gives complete dissociation or maximum molecular conductivity. If now we begin to remove the solvent (say, by evaporation) the molecular conductivity calculated for the successively increasing concentrations will remain constant up to that concentration which first gives the maximum molecular conductivity. If, however, we *should*

start with that initial great dilution and, while removing solvent, add the ions of the salt sufficiently rapidly, we should find for each successively greater concentration an increase in the molecular conductivity until that concentration is again reached which first gives the maximum value. After this the molecular conductivity must again decrease with increase in concentration.

Since the amount of polymerization of the solute molecules need only be very small in order to compensate for the effect due to ionization, as determined by the boiling-point method, we can not be far wrong in assuming that the polymerized molecules are highly dissociated and that their ionic product,

$$\overset{+}{\text{Li.S}_1} \times \overset{-}{\text{LiBr}_2}.\text{S}_5 = \text{K},$$

is relatively very large. Furthermore, according to Walden's views upon the dielectric constant, the dissociation should increase with increase in the concentration of the salt. We may consider, therefore, that those dilutions which give minimum values of molecular conductivity are far beyond the dilution at which the polymerized molecules are completely dissociated. Normally, the molecular conductivity of these should remain constant with removal of solvent until that concentration is reached which just gives the maximum value for the molecular conductivity of the polymerized solute. With the increase in concentration of the highly dissociated polymer there is an abnormally rapid increase in the number of ions with the result that, from the minimum on, the molecular conductivity increases with concentration. If it is possible to exceed the ionic product which the ions of the polymerized molecules would give at the concentration giving the maximum molecular conductivity, then from this point on the molecular conductivity should decrease with further increase in concentration.

Starting then with the most concentrated solutions, the molecular conductivity should first increase with dilution to a maximum, due to an increase in the dissociation of the solute and a decrease in the viscosity of the solution. From the maximum the molecular conductivity decreases abnormally, due to a rapid decrease in the number of ion-forming molecules which in its effect more than counterbalances the effect due to increase in dissociation. At the minimum the influences due to the two kinds of molecules and their respective dissociations just balance each other. From the minimum on the molecular conductivity continues to increase with further dilution due to the ionization of the simple salt.

A curve representing such a phenomenon would have a maximum in the concentrated regions, a minimum at higher dilutions and, if complete dissociation is possible, a second maximum at infinite dilution. The data for the molecular conductivity of tetraethylammonium iodide in aniline, when plotted, give exactly this form of curve. The same may be said for the data obtained by Franklin and Gibbs for solutions of silver nitrate in methylamine.[44] They, however, explain the phenomenon as due to the autoionization of the salt.

If, on the other hand, it is not possible to exceed the value for the ionic product at complete dissociation, the molecular conductivity should continue to increase with the concentration up to the concentration of the saturated solution. This should be true unless, perhaps, the viscosity of the solutions at these very high concentrations should be great enough to cause a decrease in conductivity. All of the most concentrated solutions in the solvents studied possess a relatively high degree of viscosity, yet for all, with the single exception of tetraethylammonium iodide, the molecular conductivity increases along with the viscosity as the concentration is increased.

Silver nitrate is the only salt that has been used in all three solvents; aniline hydrobromide has been used in aniline and quinoline. While these two can scarcely be considered as a basis for comparison, a study of their molecular conductivities brings out one or two interesting points. It will be observed that as the dielectric constant of the solvent increases the dilution at which the value of the molecular conductivity is a minimum is displaced toward solutions of higher concentration. The tendency for molecular conductivity to increase with concentration, likewise, becomes less. If this tendency is due to the presence of easily dissociating polymeric molecules, then we can say that the tendency of a solute to polymerize in different solvents becomes greater, the smaller the dielectric constant of the solvent. In the dilute solutions the molecular conductivity and, hence, the dissociation of the solute, for a given normality, increases with the dielectric constant of the solvent. In so far as these salts and solvents give us a clue, we are justified in saying that the Nernst-Thomson rule does hold for dilute solutions in solvents with low dielectric constants.

This work will be continued with solutions in other organic solvents.

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[44]loc. cit.