









# CONDUCTIVITY AND VISCOSITY IN MIXED SOLVENTS.

A STUDY OF THE CONDUCTIVITY AND VISCOSITY OF  
SOLUTIONS OF CERTAIN ELECTROLYTES IN WATER,  
METHYL ALCOHOL, ETHYL ALCOHOL, AND  
ACETONE; AND IN BINARY MIXTURES  
OF THESE SOLVENTS.

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# CONDUCTIVITY AND VISCOSITY IN MIXED SOLVENTS.

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## INTRODUCTION.

The earlier work in physical chemistry had to deal almost exclusively with aqueous solutions. This was due to the fact that water is by far the most universal solvent. It dissolves a much larger number of substances than any other known liquid. Further, water has greater power to break molecules down into ions than any other common solvent. For these reasons water is the most important solvent chemically; indeed, chemistry is largely a science of aqueous solutions.

Again, water, of all the common solvents, is the most easily obtained, and in a fair degree of purity. These are some of the reasons why solutions in water as the solvent were studied first.

During the last few years, the measurement of dissociation has been extended, to a greater or less extent, to solutions in many solvents, both inorganic and organic, and in several cases interesting and important results have been obtained.

The study of non-aqueous solutions has led to a comparison of the dissociating power of the various solvents, and this in turn has given rise to several generalizations which attempt to connect dissociating power with other physical and chemical properties of solvents.

J. J. Thomson<sup>1</sup> and Nernst<sup>2</sup> have sought to connect the dissociating power of a solvent with its dielectric constant. Nernst says:

The greater the dielectric constant of a medium, the greater becomes its electrolytic dissociation of dissolved substances under exactly similar conditions.

J. J. Thomson, after showing that molecules condensed on the surface of a conducting sphere will be completely dissociated, goes on to say:

The same effect would be produced by a substance possessing a very large specific inductive capacity. Since water is such a substance it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in solution, the forces between them are very much less than they are when the molecule is free and in the gaseous state.

Brühl<sup>3</sup> showed that while certain organic bodies, as the oximes and the alcohols, exist in a polymerized state when dissolved in hydrocarbons, chloroform, or carbon disulphide, the molecular complexes are more or less broken down in aqueous solution, and to a less extent in alcohols, ethers, esters, ketones, and phenols. All of these also exert more or less dissociating power. According to his theory of the tetravalence of oxygen they are

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<sup>1</sup> Phil. Mag., **36**, 320 (1893).

<sup>2</sup> Ztschr. phys. Chem., **13**, 531 (1894).

<sup>3</sup> Ibid., **18**, 514 (1895); **27**, 319 (1898); **30**, 1 (1899). Ber. d. chem. Gesell., **28**, 2847, 2866 (1895); **30**, 163 (1897).

unsaturated compounds, and it is to this unsaturation that he ascribes dissociating power. He also attributes the dissociating power of solvents containing nitrogen to the fact that in these compounds nitrogen exists as a triad, while it has the power of becoming pentavalent. He predicted dissociating power for compounds containing trivalent nitrogen, including the hydrazines, the amines, the diazo compounds, and liquid hydrocyanic acid; and even for other classes of unsaturated compounds, as the trichlorides of arsenic and phosphorus, the mercaptans, and alkyl sulphides. This prophecy is borne out, to some extent at least, by the later work of Walden. In his last paper Brühl sought rather to connect dissociating power with a high dielectric constant, and with the tautomerizing power of the solvent.

Ciamician<sup>1</sup> concluded that dissociating power is a function of the chemical properties of the substance, and that those substances which resemble water chemically, as methyl and ethyl alcohols, should have the greatest dissociating power.

Konowalow,<sup>2</sup> from a study of the conductivity of the compounds which amines form with acids, holds that only those solutions conduct in which there is chemical action between the solvent and the dissolved substance.

Dutoit and Aston<sup>3</sup> advanced the idea that dissociating power is related to the amount of the polymerization of the solvent. Water and the alcohols, which are good dissociants, also exist as polymerized molecules, as is shown by the surface-tension method of Ramsay and Shields.<sup>4</sup>

For further views on this subject consult the paper by Crompton.<sup>5</sup>

Donnan says:

In a solution in which the solute is more or less ionized, one might suppose the ions to be surrounded by clusters of solvent molecules which had, so to speak, condensed around them, and opposed an obstacle to their recombination. Now one might suppose this state of things as being caused by some sort of specific attraction between the solvent molecules and electricity, *i. e.*, the electrons or electrical charges which are associated with the ions. Were this the case, one might expect this specific attraction to manifest itself in other ways. For example, if electrical nuclei were present in, or were produced by any means in air which was saturated with the vapor of an ionizing liquid, then it would be just possible that the specific attraction referred to above might help to produce condensation of the vapor around these nuclei under suitable conditions, *i. e.*, if the vapor were supersaturated by a sudden adiabatic expansion. If the liquid in question did not act as an ionizing solvent, it would be natural to expect that the condensation just alluded to would only occur when the vapor entered the really unstable (*labile*) region, or at any rate would only be produced by a much higher degree of supersaturation.

From his experiments, however, he does not feel warranted in drawing any final conclusion.

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<sup>1</sup> Ztschr. phys. Chem., **6**, 403 (1890).

<sup>2</sup> Wied. Ann., **49**, 733 (1893).

<sup>3</sup> Compt. rend., **125**, 240 (1897). See also Dutoit and Friderich: Bull. Soc. Chim., [3] **19**, 325 (1898).

<sup>4</sup> Ztschr. phys. Chem., **12**, 433 (1893).

<sup>5</sup> Journ. Chem. Soc., **71**, 925 (1897).

## HISTORICAL SKETCH OF WORK IN NON-AQUEOUS SOLVENTS.

In considering more in detail the results which have led to the above generalizations, we shall consider the work done, first in inorganic solvents, second in organic solvents, and third in mixed solvents.

## INORGANIC SOLVENTS.

Water has always been regarded as the best dissociant, but recently another solvent, liquid hydrocyanic acid, has been found to produce greater dissociation.

## HYDROCYANIC ACID.

Schlundt<sup>1</sup> has measured the dielectric constant of liquid hydrocyanic acid, and found the very large value of 95 at 21°, a value which exceeds that of water, which is 80, at the same temperature. It was, therefore, important, as bearing on the Nernst-Thomson theory of dissociation, that measurements of the conductivity of solutions in this solvent be made. This has been done by Centnerszwer,<sup>2</sup> with the result that not only do solutions in hydrocyanic acid show greater conductivity, but the dissociation is also greater than in water. The substances worked with were potassium iodide and trimethylsulphonium iodide. Their conductivity at 0° was nearly the same as the conductivity of aqueous hydrochloric acid at 25°.

## WATER.

The dissociation of a great number of substances in aqueous solution has been determined by a variety of methods, including the conductivity method of Kohlrausch,<sup>3</sup> the freezing-point method of Jones,<sup>4</sup> Loomis,<sup>5</sup> and others, and the solubility method of Nernst<sup>6</sup> and Noyes.<sup>7</sup> The result of this work has been to show that for a strong acid or strong base, or a salt of a strong acid and a strong base, at a dilution of about 1000 liters the dissociation is practically complete. In most solvents, however, it is impossible to determine directly, by the conductivity method, the value of the molecular conductivity for complete ionization, since the dilution at which this is reached is so great as to preclude the application of the conductivity method. The best that we can do in these cases is to compare the values of  $\mu_v$ , at varying dilutions, with the corresponding values of  $\mu_v$  in aqueous solution. In this way an approximation to the dissociating power of various solvents can be obtained.

<sup>1</sup> Journ. Phys. Chem., **5**, 157 (1901).

<sup>2</sup> Ztschr. phys. Chem., **39**, 217 (1902).

<sup>3</sup> Wied. Ann., **26**, 160 (1885).

<sup>4</sup> Ztschr. phys. Chem., **11**, 110, 529; **12**, 623 (1893).

<sup>5</sup> Wied. Ann., **51**, 500 (1894); **57**, 495, 591 (1896); **60**, 523 (1897).

<sup>6</sup> Ztschr. phys. Chem., **4**, 372 (1889).

<sup>7</sup> Ibid., **6**, 241 (1890); **9**, 603 (1892); **12**, 162 (1893); **16**, 125 (1895).

## AMMONIA.

Several years ago Cady<sup>1</sup> noticed that solutions of salts in liquid ammonia conduct the current. Goodwin and Thomson<sup>2</sup> made some measurements of the conductivity of such solutions, while at work on the dielectric constant of liquid ammonia. The most elaborate work, however, on this subject is that of Franklin and Kraus.<sup>3</sup> They measured the conductivity of potassium bromide and nitrate, sodium bromide and bromate, ammonium chloride and nitrate, silver iodide and cyanide, besides other inorganic salts, and organic compounds over very great changes in dilution.

A direct comparison of the values of the conductivities in liquid ammonia with similar values in water, shows that the former are much larger than the latter. This, however, does not necessarily mean a larger dissociation, since the conductivity is dependent on two factors, namely, the dissociation and the velocity of the ions. The percentage dissociation ( $\alpha = \frac{\mu_v}{\mu_\infty}$ ) is larger in water than in ammonia, and hence the large conductivity of solutions in liquid ammonia is due rather to the high velocity of the ions than to the large number present.

## NITRIC ACID.

The only work on solutions in nitric acid is that of Bouty,<sup>4</sup> who has measured the conductivity of certain alkaline nitrates when dissolved in nitric acid. The conductivities are nearly as large as in water, but the work is too fragmentary to permit making comparisons between the dissociating power of nitric acid and of water. The former is, however, in all probability, a good dissociant.

## SULPHUR DIOXIDE.

Walden and Centnerszwer<sup>5</sup> published the results of an extensive investigation on sulphur dioxide as a solvent. This is an extension of the older work of Walden.<sup>6</sup> They investigated the conductivity of nineteen salts, consisting of iodides, bromides, chlorides, and sulphocyanates of inorganic and organic bases. They show, first, that while in aqueous solution the molecular conductivities at 25° of monobasic halogen salts generally lie between 100 and 140, the corresponding values in sulphur dioxide vary between 3 and 157; second, that Kohlrausch's law of the independent migration velocities of the ions does not hold for solutions in sulphur dioxide. They have also shown by a series of conductivity measurements at different temperatures between -78° and 157° (the freezing-point and critical temperature of

<sup>1</sup> Journ. Phys. Chem., **1**, 707 (1896).

<sup>2</sup> Phys. Rev., **8**, 38 (1899).

<sup>3</sup> Amer. Chem. Journ., **23**, 277; **24**, 83 (1900).

<sup>4</sup> Compt. rend., **106**, 595 (1888).

<sup>5</sup> Ztschr. phys. Chem., **39**, 513 (1902).

<sup>6</sup> Ber. d. chem. Gesell., **32**, 2862 (1899).

sulphur dioxide), that the molecular conductivity at first increases with the temperature, passes through a maximum, and then diminishes as the critical temperature is approached. This is seen at once to be just what would be expected from the polymerized solvent theory of Dutoit and Aston. As the temperature rises the association of the solvent decreases, and this would be expected to diminish the ionizing power. They have also determined the molecular weights of a number of electrolytes (salts) in liquid sulphur dioxide, by the boiling-point method; reaching the remarkable result that many of these salts show a molecular weight greater than normal, or what is the same thing, the value of the van't Hoff coefficient "i" is less than unity. This they endeavor to show is due to the fact that, in addition to the electrolytic dissociation, an association takes place in the solutions in sulphur dioxide. Facts similar to the above were noticed by Franklin and Kraus<sup>1</sup> in their work on liquid ammonia.

The remaining work in inorganic solvents we owe chiefly to Walden.<sup>2</sup> He has investigated the solvent and ionizing power of the following compounds: Phosphorus trichloride, phosphorus tribromide, phosphorus oxychloride, arsenic trichloride, antimony trichloride, antimony pentachloride, boron trichloride, silicon tetrachloride, tin tetrachloride, sulphur monochloride, sulphuryl chloride, thionyl chloride, sulphur trioxide, and liquid bromine. Of these, sulphur monochloride, sulphuryl chloride, thionyl chloride, phosphorus oxychloride, arsenic trichloride, and antimony trichloride show considerable ionizing power, while solutions in the remaining solvents exhibit only the very slightest conductivity. In his next paper Walden adds a study of arsenic tribromide, chlorosulphuric acid, sulphuric acid, and the dimethyl ester of sulphuric acid. All of these show a strong tendency to ionize dissolved electrolytes. It is important to notice from this work of Walden that there appears to be no connection between dissociating power and chemical constitution. Antimony pentachloride does not dissociate electrolytes, while the trichloride dissociates to a very considerable extent. On the other hand, phosphorus trichloride does not dissociate, while phosphorus oxychloride does. It is thus evident that, among the inorganic solvents at least, a knowledge of the dissociating power of one solvent tells us nothing as to the dissociating power of substances closely related chemically.

Oddo<sup>3</sup> has also shown that phosphorus oxychloride strongly ionizes electrolytes. Tolloczko,<sup>4</sup> as well as Garelli and Bassani,<sup>5</sup> have worked with the halides of arsenic and antimony, showing them to have ionizing power.

<sup>1</sup> Amer. Chem. Journ., **20**, 836 (1898); **24**, 83 (1900).

<sup>2</sup> Ztschr. anorg. Chem., **25**, 209 (1900); **29**, 371 (1903).

<sup>3</sup> Atti R. Accad. dei Lincei Roma, [5] **10** 452.

<sup>4</sup> Ztschr. phys. Chem., **30**, 705 (1899).

<sup>5</sup> Atti R. Accad. dei Lincei Roma, [5] **10** 255.

Kahlenberg and Lincoln<sup>1</sup> studied solutions of ferric chloride, antimony trichloride, bismuth trichloride, and mercuric chloride in phosphorus trichloride and arsenic trichloride, with results which confirm those mentioned above. Centnerszwer<sup>2</sup> is authority for placing cyanogen among the solvents that do not dissociate. Frankland and Farmer<sup>3</sup> have also shown that nitrogen peroxide does not dissociate, while Skilling<sup>4</sup> demonstrates that solutions in hydrogen sulphide show no conductivity.

The following table of inorganic solvents is given to show what relations exist between dissociating power, dielectric constants, and the association factor:

TABLE 1. — *Inorganic solvents which effect dissociation.*

Solvent.	Dielectric constant.	Association factor.	Considered as —
Hydrocyanic acid . . . . .	95	(?)	Saturated.
Water . . . . .	81.12	3.7	Do.
Ammonia . . . . .	16.2	1.0	Unsaturated.
Sulphur dioxide . . . . .	13.75	1.0	Do.
Nitric acid . . . . .	(?)	1.7-1.9	Saturated.
Arsenic trichloride . . . . .	12.35	(?)	Unsaturated.
Arsenic tribromide . . . . .	(?)	(?)	Do.
Phosphorus oxychloride . . . . .	13.9	1.00	Saturated.
Antimony trichloride . . . . .	33.2	(?)	Unsaturated.
Thionyl chloride . . . . .	9.05	1.08	Do.
Sulphuryl chloride . . . . .	9.15	0.97	Saturated.
Dimethyl sulphate . . . . .	(?)	(?)	Do.
Chlorsulphuric acid . . . . .	(?)	(?)	Do.
Sulphuric acid . . . . .	(?)	32.0	Do.
Sulphur monochloride . . . . .	4.8	0.95-1.05	Unsaturated.
<i>Inorganic solvents which do not dissociate electrolytes.</i>			
Bromine . . . . .	3.18	1.2-1.3	Saturated.
Cyanogen . . . . .	2.52	(?)	Do.
Sulphur trioxide . . . . .	3.56	.....	Do.
Boron trichloride . . . . .	(?)	(?)	Do.
Phosphorus trichloride . . . . .	3.36	1.02	Unsaturated.
Phosphorus tribromide . . . . .	(?)	(?)	Do.
Antimony pentachloride . . . . .	3.78	(?)	Saturated.
Silicon tetrachloride . . . . .	(?)	1.06	Do.
Tin tetrachloride . . . . .	3.2	(?)	Do.
Hydrogen sulphide . . . . .	(?)	(?)	Do.
Nitrogen peroxide . . . . .	(?)	(?)	Do.

The values for the association factors are taken from the researches of Ramsay and Shields,<sup>5</sup> and Ramsay and Aston;<sup>6</sup> while those for the dielectric constants are almost wholly taken from the work of Turner.<sup>7</sup>

<sup>1</sup> Journ. Phys. Chem., **3**, 12 (1899).

<sup>2</sup> Ztschr. phys. Chem., **39**, 217 (1902).

<sup>3</sup> Journ. Chem. Soc., **79**, 1356 (1901).

<sup>4</sup> Amer. Chem. Journ., **26**, 383 (1901).

<sup>5</sup> Ztschr. phys. Chem., **12**, 433 (1893).

<sup>6</sup> Journ. Chem. Soc., **65**, 167 (1894).

<sup>7</sup> Journ. Phys. Chem., **5**, 503 (1901).



## ORGANIC SOLVENTS.

## HYDROCARBONS.

Kahlenberg and Lincoln<sup>1</sup> have shown that solutions of ferric chloride in a large number of hydrocarbons do not conduct the current, while Kablukoff<sup>2</sup> showed that the conductivity of hydrochloric acid in benzene, xylene, and hexane is very small. This is in perfect accord with what would be expected from the fact that non-electrolytes dissolved in hydrocarbons tend, in a number of cases, to give a complex molecular weight when this is determined by the boiling-point or freezing-point method.

## ALCOHOLS.

When we come to study the work on solutions in the alcohols, we find that a considerable amount has been done, especially in the case of the two lowest members of the aliphatic series. Fitzpatrick<sup>3</sup> studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride, and calcium chloride in methyl alcohol, and found values which, though less than in water, were very considerable. Hartwig<sup>4</sup> measured the conductivity of formic, acetic, and butyric acids in methyl alcohol. Paschow<sup>5</sup> studied the conductivities in methyl alcohol of potassium iodide, cadmium iodide, calcium nitrate, and potassium and sodium acetates. Völlmer<sup>6</sup> worked out the conductivities of potassium and sodium iodides, potassium and sodium acetates, and lithium chloride in methyl alcohol, over a considerable range of dilution.

Holland<sup>7</sup> studied the effect of non-electrolytes on the conductivity in methyl alcohol of potassium, sodium, calcium, lithium, and ammonium nitrates, and sodium chloride.

Carrara<sup>8</sup> carried out by far the most extensive investigation which has yet been made of salts in methyl alcohol. He measured the conductivities of the following substances at various dilutions: Potassium chloride, bromide, iodide, methylate; sodium chloride, iodide, methylate, acetate; lithium chloride; ammonium chloride, bromide, iodide, fluoride; tetraethylammonium chloride, bromide, iodide; tetramethylammonium iodide; triethylamine, diisopropylamine, and a number of sulphur derivatives. Kerler,<sup>9</sup> working in Beckmann's laboratory, determined the conductivities of lithium and calcium chlorides; lithium, sodium, and barium bromides; potassium iodide, ammonium nitrate, and potassium acetate. The conductivity of

<sup>1</sup> Journ. Phys. Chem., **3**, 12 (1899).

<sup>2</sup> Ztschr. phys. Chem., **4**, 429 (1889).

<sup>3</sup> Phil. Mag., **24**, 378 (1887).

<sup>4</sup> Wied. Ann., **33**, 58 (1888); **43**, 838 (1891).

<sup>5</sup> Charkow, 1892.

<sup>6</sup> Wied. Ann., **52**, 328 (1894).

<sup>7</sup> Ibid., **50**, 263.

<sup>8</sup> Gazz. Chim. Ital., **26**, [1] 119 (1896).

<sup>9</sup> Dissertation Erlangen (1894).

mercuric iodide in methyl alcohol was measured by Cattaneo;<sup>1</sup> Schall<sup>2</sup> determined the conductivity of hydrochloric, picric, oxalic, and dichloroacetic acids in methyl alcohol; Kablukoff<sup>3</sup> also studied the conductivity of hydrochloric acid in methyl alcohol, and Kahlenberg and Lincoln<sup>4</sup> measured the conductivity of ferric chloride and antimony trichloride in this solvent. The most satisfactory work on the whole that has ever been done on the conductivity of solutions in methyl alcohol is that of Zelinsky and Krapiwín.<sup>5</sup> Their work included a number of salts in pure methyl alcohol, as well as in a mixture of this solvent and water, as we shall see later. They used in their work potassium bromide and iodide, ammonium bromide and iodide, cadmium iodide, tetramethylammonium bromide and iodide, tetraethylammonium iodide, a number of the substituted amines and sulphines, diethyl- and triethyl-stannic iodides, "fumaroid" dimethylsuccinic acid, oxalic acid, iodic acid, and trichloroacetic acid.

Jones<sup>6</sup> has applied his boiling-point apparatus to the determination of the dissociation of salts in methyl alcohol. The salts used were: Potassium, sodium, and ammonium bromides; potassium, sodium, and ammonium iodides; potassium and sodium acetates, and calcium nitrate. The dissociation in methyl alcohol, as found by the boiling-point method, is about two-thirds of that in water under the same conditions.

#### ETHYL ALCOHOL.

A considerable amount of work has also been done in ethyl alcohol. The conductivity of the following substances has been determined by Fitzpatrick:<sup>7</sup> Calcium chloride, calcium nitrate, lithium chloride, lithium nitrate, mercuric, magnesium, and ferric chlorides. Hartwig<sup>8</sup> has determined the conductivity of formic, acetic, and butyric acids in alcohol. Vicentini<sup>9</sup> worked on the chlorides of ammonium, lithium, magnesium, calcium, cadmium, zinc, and copper. Cattaneo<sup>10</sup> has studied the conductivities of ferrous, ferric, and mercuric chlorides, and cadmium bromide and iodide. He found that these substances have a negative temperature coefficient of conductivity. Völlmer used a larger number of salts in ethyl alcohol than he did in water.<sup>11</sup> These were potassium and sodium iodides, potassium and sodium acetates, sodium, lithium, and calcium chlorides, and calcium and silver nitrates. Kawalki,<sup>12</sup> by a comparison of the rates of diffusion of a series of salts in water and in ethyl alcohol, showed that the rates of diffusion

<sup>1</sup> Rend. R. Acc. Linc. Roma (1895).

<sup>2</sup> Ztschr. phys. Chem., **14**, 701 (1894).

<sup>3</sup> Ibid., **4**, 429 (1889).

<sup>4</sup> Journ. Phys. Chem., **3**, 26 (1899).

<sup>5</sup> Ztschr. phys. Chem., **21**, 35 (1896).

<sup>6</sup> Ibid., **31**, 114 (1899).

<sup>7</sup> Phil. Mag., **24**, 378 (1887).

<sup>8</sup> Wied. Ann., **33**, 58 (1888); **43**, 838 (1891).

<sup>9</sup> Biebl. Wied. Ann., **9**, 131 (1885).

<sup>10</sup> Ibid., **18**, 219, 365 (1894).

<sup>11</sup> Wied. Ann., **52**, 328 (1894).

<sup>12</sup> Ibid., **52**, 324 (1894).

in the two solvents bear the same relation to one another as the maximum molecular conductivities in the two solvents. Reference should be made to the work of Paschkow,<sup>1</sup> who measured the conductivities in ethyl alcohol, of potassium and cadmium iodides, potassium and sodium acetates, and calcium nitrate; of Schall,<sup>2</sup> who used picric, oxalic, and dichloroacetic acids; of Wildermann,<sup>3</sup> who studied the conductivities of di- and tri-chloroacetic acids; of Kahlenberg and Lincoln,<sup>4</sup> who worked with ferric chloride and antimony trichloride in ethyl alcohol; and of Kablukoff,<sup>5</sup> who has measured the conductivity of hydrochloric acid in ethyl alcohol.

Jones<sup>6</sup> measured the dissociation of a number of salts in ethyl alcohol, using the boiling-point method. These include potassium and sodium iodides, sodium and ammonium bromides, potassium and sodium acetates, and calcium nitrate. These salts were found to be dissociated by ethyl alcohol, to from one-third to one-fourth the extent that they are dissociated in water at the same dilution. It should be observed, however, that dissociation as measured by the boiling-point method would not seem to be directly comparable with dissociation as measured by conductivity, since the two sets of measurements are made at different temperatures. It has, however, been established by Jones and Douglas,<sup>7</sup> and later confirmed by Noyes and Coolidge<sup>8</sup> and Jones and West,<sup>9</sup> that the temperature coefficient of dissociation is, in aqueous solutions, small; in which case, if this holds for alcoholic solutions, there should be only a very small difference between the results obtained by the two methods.

#### HIGHER ALCOHOLS.

Comparatively little work has been done on the dissociating power of the higher alcohols. Schlamp<sup>10</sup> has shown, from the results of his measurements on solutions of lithium and calcium chlorides, sodium iodide, and lithium salicylate, that their conductivity in propyl alcohol is somewhat less than one-half that in ethyl alcohol.

In propyl and amyl alcohols Carrara<sup>11</sup> has made a few measurements, while Hartwig<sup>12</sup> determined the conductivity of formic, acetic, and butyric acids in amyl alcohols. Among the isoalcohols Carrara<sup>13</sup> worked with isopropyl, and Kablukoff<sup>14</sup> with isobutyl and isoamyl alcohols, obtaining the remarkable result that in isoamyl alcohol solution the molecular conductivity of hydrochloric acid *decreases with increase in dilution*. Schall<sup>15</sup> has determined the conductivity of picric acid in isobutyl alcohol.

<sup>1</sup> Dissertation, Charkow, 1892.

<sup>2</sup> Ztschr. phys. Chem., **14**, 701 (1894).

<sup>3</sup> Ibid., **14**, 267 (1894).

<sup>4</sup> Journ. Phys. Chem., **3**, 26 (1899).

<sup>5</sup> Ztschr. phys. Chem., **4**, 429 (1889).

<sup>6</sup> Ibid., **31**, 133 (1899).

<sup>7</sup> Amer. Chem. Journ., **26**, 428 (1901).

<sup>8</sup> Ztschr. phys. Chem., **46**, 323 (1903).

<sup>9</sup> Amer. Chem. Journ., **34**, 357 (1905).

<sup>10</sup> Ztschr. phys. Chem., **14**, 272 (1894).

<sup>11</sup> Gazz. Chim. Ital., **27**, I, 221 (1897).

<sup>12</sup> Wied. Ann., **33**, 48 (1888); **43**, 838 (1891).

<sup>13</sup> Gazz. Chim. Ital., **27**, I, 221 (1897).

<sup>14</sup> Ztschr. phys. Chem., **4**, 432 (1889).

<sup>15</sup> Ibid., **14**, 707 (1894).

## ETHER.

Practically the only work on ethereal solutions is that of Cattaneo<sup>1</sup> and Kablukoff.<sup>2</sup> Cattaneo measured the conductivity of ethereal solutions of cadmium iodide, cadmium bromide, ferrous and ferric chlorides, aluminium mercurous and stannous chlorides, salicylic and hydrochloric acids. He found that ethereal solutions have a negative temperature coefficient of conductivity, and that the molecular conductivity of hydrochloric acid in ether decreased with increase in dilution. This is analogous to the results of Kablukoff in the case of isoamyl alcohol. Indeed, Kablukoff found also that the conductivity of hydrochloric acid decreased with the dilution.

## KETONES.

The conductivity of a number of salts of the alkalis in acetone were published by Cattaneo<sup>3</sup> several years ago. About the same time a paper appeared from St. v. Lasczynski<sup>4</sup> on the conductivity of some salts in acetone. Among these were included lithium and mercuric chlorides, potassium iodide, silver nitrate, and potassium, sodium, and ammonium sulphocyanates. The conductivity of solutions in acetone has also been measured by Carrara.<sup>5</sup>

Kahlenberg and Lincoln<sup>6</sup> measured the conductivity of solutions of ferric, cupric, and stannous chlorides, and antimony trichloride in acetone; and Dutoit and Aston,<sup>7</sup> as well as Dutoit and Friderich,<sup>8</sup> studied a number of solutions in acetone and other ketones. Dutoit and Aston pointed out, as has been mentioned, that those solvents which dissociate to the greatest extent are polymerized, as shown by the surface-tension method of Ramsay and Shields.<sup>9</sup>

In addition to acetone they worked with methylethyl ketone and methylpropyl ketone. In the former solvents they used mercuric chloride, cadmium iodide, ammonium sulphocyanate, and sodium salicylate; in the latter, cadmium iodide, ammonium sulphocyanate, and sodium salicylate. They found that in the methylethyl ketone the conductivities were larger than in the methylpropyl ketone, but that the conductivity in acetone was the greatest of the three. Dutoit and Aston conclude from their work, together with that of Kablukoff,<sup>10</sup> that there is a general relation between the polymerization of the molecules of a solvent and its dissociating power.

<sup>1</sup> Atti R. Acc. del le Scienze, Torino, **28**, 329. Rend. R. Accad. dei Lincei, [5] **2**, 295.

<sup>2</sup> Ztschr. phys. Chem., **4**, 431 (1889).

<sup>3</sup> Rend. R. Accad. dei Lincei, [5] **4**<sup>o</sup>, 2 sem., 63-75.

<sup>4</sup> Ztschr. Elektrochem., **2**, 55 (1895).

<sup>5</sup> Gazz. Chim. Ital., **27**, I, 207 (1897).

<sup>6</sup> Journ. Phys. Chem., **3**, 27 (1899).

<sup>7</sup> Compt. rend., **125**, 240 (1897).

<sup>8</sup> Bull. Soc. Chim., [3] **19**, 321 (1897).

<sup>9</sup> Ztschr. phys. Chem., **12**, 423 (1893).

<sup>10</sup> Ibid., **19**, 251 (1896).

In connection with their work in acetone they make the following remarkable statement:

We have found by the boiling-point method that the following salts in acetone have normal molecular weights: Cadmium iodide, lithium chloride, sodium iodide, mercuric chloride, and ammonium sulphocyanate.

And that these substances in acetone conduct the current. Results<sup>1</sup> obtained in the physical-chemical laboratory of the Johns Hopkins University indicate that this statement is erroneous.

#### ACIDS.

The dissociating power of formic acid has been quite elaborately investigated by Zanninovich-Tessarini.<sup>2</sup> In his work he used mainly the freezing-point method, but also studied the conductivity of a few salts in this solvent. He measured the freezing-point lowering of formic acid produced by the following substances, at dilutions varying from 0.34 to 3.4 normal (and in some cases at even greater concentration): Potassium, sodium, ammonium, and lithium chlorides; potassium, sodium, and ammonium bromides; hydrochloric, acetic, and trichloroacetic acids. Formic acid is one of the strongest dissociating solvents next to hydrocyanic acid and water. The behavior of hydrochloric acid in this solvent is very remarkable. Not only does it show no dissociation, but the molecules are actually polymerized. Although, as just mentioned, the freezing-point lowering showed no dissociation, the conductivity in this solvent was very considerable. This may be due to the fact that while a majority of the molecules were polymerized, some were dissociated into ions which conducted the current. The conductivities of potassium and sodium chlorides in this solvent were also found to be very large.

Zanninovich-Tessarini<sup>3</sup> has also determined the freezing-point lowering produced by sodium bromide and lithium chloride in acetic acid. The former gave normal values, indicating no dissociation; while the latter showed marked polymerization.

The conductivity of sulphuric acid in acetic acid has been measured by Jones,<sup>4</sup> who found that the molecular conductivity, which was small at all dilutions, increased with the dilution to a certain point, and then decreased with further increase in the dilution of the solution. This is somewhat analogous to the result obtained by Kablukoff<sup>5</sup> for hydrochloric acid in ether and in isoamyl alcohol.

#### THE NITRILES AND CYANOGEN.

Dutoit and Aston<sup>6</sup> determined the conductivities of mercuric chloride, sodium bromide, cadmium bromide and iodide, ammonium sulphocyanate, and silver nitrate, in propionitrile. The investigation was extended by

<sup>1</sup> Amer. Chem. Journ., **27**, 16 (1902).

<sup>2</sup> Ztschr. phys. Chem., **19**, 251 (1896).

<sup>3</sup> Ibid., **19**, 255 (1896).

<sup>4</sup> Amer. Chem. Journ., **16**, 13 (1894).

<sup>5</sup> Loc. cit.

<sup>6</sup> Compt. rend., **125**, 240 (1897).

Dutoit and Friderich<sup>1</sup> to solutions in acetonitrile and butyronitrile. It was shown that the dissociating power is greater in the first members of the nitriles, but in no case do they at all approach the dissociating power of liquid hydrocyanic acid as determined by the recent work of Centnerszwer.<sup>2</sup>

Centnerszwer<sup>3</sup> has also shown that liquid cyanogen is a non-dissociant.

#### PYRIDINE.

Werner<sup>4</sup> found that certain inorganic salts, when dissolved in pyridine, conduct the current very well, but show very little or no dissociation by the boiling-point method. It is, however, to the work of St. v. Laszczynski and St. v. Gorski<sup>5</sup> that we owe what knowledge we have of the dissociating power of pyridine. They measured the conductivity of lithium chloride, potassium, sodium, and ammonium iodides, and potassium, sodium, and ammonium sulphocyanates in pyridine, over a wide range of dilutions.

#### OTHER ORGANIC SOLVENTS.

Such a few measurements have been made in other organic solvents that they can be passed over with brief reference. Thus, Werner<sup>6</sup> found that cuprous chloride in ethyl sulphide conducts very poorly. Cattaneo<sup>7</sup> studied a few solutions in glycerol, and found that they had a larger conductivity than the corresponding solutions in ether. They also had larger temperature coefficients of conductivity. Dutoit and Aston<sup>8</sup> measured the conductivities of electrolytes in benzene chloride, ethyl bromide, and amyl acetate, and found that these solutions conduct very poorly. They found, on the other hand, that solutions in nitroethane conduct very well. Dutoit and Friderich<sup>9</sup> worked with acetophenone as a solvent, and with cadmium iodide, mercuric chloride, and ammonium sulphocyanate as electrolytes. The conductivity in this solvent was very small.

Four other solvents have thus far been employed; namely, ethyl acetate, benzaldehyde, ethyl acetoacetate, and nitrobenzene. This work was done by Kahlenberg and Lincoln.<sup>10</sup> As electrolytes they used ferric and stannous chlorides, bismuth trichloride, and antimony trichloride. The conductivities in these solvents are in general small, but vary considerably with the nature of the electrolyte used.

The most recent work in organic solvents is that of Walden.<sup>11</sup> Five large pieces of work, yielding important and interesting results, have recently been published. A large number of types of organic compounds have been

<sup>1</sup> Bull. Soc. Chim., [3] **19**, 321 (1898).

<sup>2</sup> Ztschr. phys. Chem., **39**, 217 (1902).

<sup>3</sup> Loc. cit.

<sup>4</sup> Ztschr. anorg. Chem., **15**, I, 39 (1897).

<sup>5</sup> Ztschr. Elektrochem., **4**, 290 (1897).

<sup>6</sup> Ztschr. anorg. Chem., **15**, I, 139 (1897).

<sup>7</sup> Beibl. Wied. Ann., **17**, 365 (1893).

<sup>8</sup> Compt. rend., **125**, 240 (1897).

<sup>9</sup> Bull. Soc. Chim., [3] **19**, 325 (1898).

<sup>10</sup> Journ. Phys. Chem., **3**, 12 (1899).

<sup>11</sup> Ztschr. phys. Chem., **46**, 103 (1903); **54**, 129 (1906); **55**, 207 (1906); **55**, 281 (1906); **55**, 682 (1906); **58**, 479 (1907); **59**, 192 (1907).

brought within the scope of these investigations. These include alcohols, aldehydes, acids, acid anhydrides, esters, acid amides and amines, nitriles, sulphocyanates, mustard oils, nitro-compounds, nitrosodimethylene, ethald-oxime, epichlorhydrine, and ketones.

The work has had to do with the conductivity of electrolytes in these solvents, with the relation between conductivity and internal friction, with boiling-point determinations, and with the solvent power of these different substances. For details the original papers must be consulted.

## MIXED SOLVENTS.

## HYDROGEN DIOXIDE AND WATER.

The dielectric constant of a mixture of hydrogen dioxide and water is greater than that of pure water. This has been shown by Calvert,<sup>1</sup> and would lead one to suspect that electrolytes dissolved in such mixtures would have a greater conductivity than in pure water, in accordance with the Thomson-Nernst rule. The dissociating power of such mixtures has, however, not yet been determined. Reference should also be made to the later work of Calvert,<sup>2</sup> showing that hydrogen dioxide has acid properties, and to the work of Jones, Barnes, and Hyde<sup>3</sup> along the same line.

## MIXTURES OF WATER AND THE ALCOHOLS.

Only brief mention need be made of the work of Lenz,<sup>4</sup> Kerler,<sup>5</sup> Stephan,<sup>6</sup> Kablukoff,<sup>7</sup> Carrara,<sup>8</sup> Schall,<sup>9</sup> and Arrhenius.<sup>10</sup> Wakeman,<sup>11</sup> in quite an elaborate investigation, measured the conductivity of organic acids in mixtures of ethyl alcohol and water in varying proportions. The results show that the conductivity becomes gradually smaller as the amount of alcohol becomes larger and larger. This is just what would be expected from the relative conductivities in these two solvents.

Zelinsky and Krapiwins<sup>12</sup> have, however, obtained results of a very different character. They found that the salts with which they worked, when dissolved in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol, gave a conductivity considerably less than the conductivity in either alcohol or water.

Similar results were obtained by Cohen<sup>13</sup> with ethyl alcohol and water, but only when the mixture contained very little water, and at dilutions which were quite large, as is shown by table 2.

<sup>1</sup> Ann. der Phys., **1**, 483 (1900).

<sup>2</sup> Ztschr. phys. Chem., **38**, 513 (1901).

<sup>3</sup> Amer. Chem. Journ., **27**, 22 (1902).

<sup>4</sup> Mém. de l'Acad. de St. Pétersbourg, [7] **30**, 1881.

<sup>5</sup> Dissertation Erlangen, 1884.

<sup>6</sup> Wied. Ann., **17**, 673 (1882).

<sup>7</sup> Ztschr. phys. Chem., **4**, 432 (1889).

<sup>8</sup> Gazz. Chim. Ital., **16**, 1 (1886).

<sup>9</sup> Ztschr. phys. Chem., **14**, 701 (1894).

<sup>10</sup> Ibid., **9**, 487 (1892).

<sup>11</sup> Ibid., **11**, 49 (1893).

<sup>12</sup> Ibid., **21**, 35 (1896).

<sup>13</sup> Ibid., **25**, 31 (1898).

TABLE 2. — *Potassium iodide.*

$v$	Pure alcohol. $\mu_v 18^\circ$	80 p. ct. alcohol. $\mu_v 18^\circ$	$v$	Pure alcohol. $\mu_v 18^\circ$	80 p. ct. alcohol. $\mu_v 18^\circ$
64	26.1	30.9	512	34.4	34.1
128	29.2	32.2	1024	36.0	34.5
256	31.8	33.2	2048	36.3	35.0

From an examination of the above results it is seen that the conductivities in the mixtures of water and alcohol are the greater until a dilution of 512 liters is reached. At higher dilutions the conductivity in the pure alcohol becomes greater than that of the alcohol containing 20 per cent of water. In general, however, Cohen found that addition of water increased the conductivity, as we should expect.

Lenz<sup>1</sup> measured the conductivities of various salts (potassium iodide, bromide, and chloride, sodium chloride, etc.) in mixtures of methyl and ethyl alcohols and water. He found that in certain cases the relative resistances can be obtained from the equation

$$r = 100(1 + bv)$$

where 100 is taken as the resistance of an aqueous solution of the same per cent,  $v$  is the volume per cent of alcohol, and  $b$  a constant. The formula holds best for the mixtures of methyl alcohol and water.

Stephan<sup>2</sup> studied the conductivities of dilute solutions of sodium, potassium and lithium chlorides, and sodium and potassium iodides in mixtures of ethyl alcohol and water.

Kablukoff<sup>3</sup> determined the conductivity of hydrochloric acid in ethyl alcohol containing varying amounts of water.

Arrhenius<sup>4</sup> investigated the changes in the conductivity of aqueous solutions, resulting from the addition to them of small quantities (less than 10 per cent by volume) of non-electrolytes, such as methyl or ethyl alcohol, cane-sugar, acetone, etc. He found that the changes could be expressed by the empirical formula —

$$l = l_0 \left( 1 + \frac{a}{x} \right)^2$$

where  $l$  is the conductivity in water,  $l_0$  that in the mixture,  $x$  the volume per cent of added non-electrolyte, and  $a$  a constant peculiar to each non-electrolyte. Where two non-electrolytes were added a similar empirical formula was found to hold. The coefficient  $a$  differs not only for different

<sup>1</sup> Mém. de l'Acad. de St. Pétersbourg, 7, 30 (1881).

<sup>2</sup> Wied. Ann., 17, 673 (1882).

<sup>3</sup> Ztschr. phys. Chem., 4, 432 (1889).

<sup>4</sup> Ibid., 9, 487 (1892).



non-electrolytes and different electrolytes, but varies also with concentration, and is greatest when dissociation is least.

Arrhenius concludes that the amount of dissociation is not appreciably changed by addition of small quantities of non-electrolytes. This follows from the fact that the alteration in conductivity is independent of the concentration. Further, he found that the velocity of inversion of cane-sugar is not appreciably influenced by addition of small amounts of non-electrolytes.

Holland<sup>1</sup> worked in the same field as did Arrhenius. His results will be referred to again. Strindberg<sup>2</sup> repeated and confirmed some of Arrhenius's work.

Wakeman<sup>3</sup> measured the conductivities of various electrolytes, sodium and potassium chlorides, hydrochloric acid, and numerous organic acids, in mixtures of ethyl alcohol and water (containing 10, 20, 30, 40, and 50 per cent of alcohol).

For the cases studied, the equation —

$$\frac{\Delta}{p(100 - p)} = \text{constant}$$

was found to hold, where  $\Delta$  is the difference between the conductivity of the electrolyte in water and in the mixture, respectively, and  $p$  is the per cent of alcohol by volume.

Schall<sup>4</sup> determined the conductivity of picric acid in aqueous alcohol.

Zelinsky and Krapiwín<sup>5</sup> studied the conductivities of sodium and ammonium iodides and bromides in water, methyl alcohol, and a mixture of the two containing 50 per cent of water by weight; for dilutions from  $v = 16$  to  $v = 1024$ . Here a striking phenomenon was observed. The conductivities in the 50 per cent mixture were found to be decidedly less than the corresponding conductivities in the pure solvents. This minimum is best seen when the results are plotted as curves, with the conductivities as ordinates and the composition of the mixture as abscissæ.

Cohen<sup>6</sup> observed the minimum in the case of potassium iodide. He made a study of the conductivity of potassium iodide in mixtures of ethyl alcohol and water (containing 20, 40, 60, 80, and 99 per cent alcohol). The dilutions ranged from  $v = 64$  to  $v = 2048$ . The minimum manifested itself in the 80 per cent mixture beyond the concentration  $v = 512$ .

From his own observations, and from those of Wakeman (*loc. cit.*), he concludes that the relation

$$\frac{\mu_v \text{H}_2\text{O}}{\mu_v \text{H}_2\text{O} \cdot \text{Alc.}} = \text{constant}$$

<sup>1</sup> Wied. Ann., **50**, 261 (1893).

<sup>2</sup> Ztschr. phys. Chem., **14**, 161 (1894).

<sup>3</sup> *Ibid.*, **11**, 49 (1893).

<sup>4</sup> *Ibid.*, **14**, 701 (1894).

<sup>5</sup> *Ibid.*, **21**, 35 (1896).

<sup>6</sup> *Ibid.*, **25**, 31 (1898).

holds, being independent of both temperature and concentration; that is, the conductivities compared are approaching a limiting value at the same rate, and either the dissociation is the same in the cases compared, or for mixtures of alcohol and water conductivity is not a direct measure of dissociation. Cohen is inclined to the latter view.

Walker and Hambly<sup>1</sup> studied the conductivity of diethylammonium hydrochloride in mixtures of water and ethyl alcohol.

Hantzsch<sup>2</sup> made some interesting applications of results obtained by studying conductivities in various mixtures.

Tijmstra<sup>3</sup> investigated the conductivities of solutions obtained by the action of mixtures of methyl or ethyl alcohol and water on sodium. In the case of the mixtures of methyl alcohol and water the minimum was observed.

Roth<sup>4</sup> made a careful study of the conductivity of potassium chloride in mixtures of ethyl alcohol and water containing 8 and 20 per cent alcohol by weight. He found that the relation given by Wakeman (*loc. cit.*) holds, while that given by Cohen (*loc. cit.*) does not. The quotient—

$$\frac{\mu_v \text{H}_2\text{O}}{\mu_v \text{H}_2\text{O} \cdot \text{Alc.}}$$

was found to decrease with increasing dilution, and with increase in the amount of alcohol in the mixture. This, Roth thinks, may indicate a decrease in dissociation. The relation given by Arrhenius (*loc. cit.*) was also found to be valid.

The work of Wolf<sup>5</sup> and of Rudorf<sup>6</sup> needs no special consideration.

#### CONDUCTIVITY AND VISCOSITY.

That viscosity and conductivity are related is by no means a new idea. As early as 1856, G. Wiedemann<sup>7</sup> studied aqueous solutions of copper sulphate, and concluded that the conductivity of a solution is directly proportional to the concentration, and inversely proportional to the viscosity. When formulated this would be

$$\frac{K\eta}{p} = \text{constant}$$

where  $K$  is the conductivity of the solution of concentration  $p$ , and  $\eta$  the viscosity.

Grottrian,<sup>8</sup> in 1876, measured the conductivity and viscosity of solutions at different temperatures, but obtained indecisive results.

<sup>1</sup> Journ. Chem. Soc., **71**, 61 (1899).

<sup>2</sup> Ztschr. anorg. Chem., **25**, 332 (1900).

Ber. d. chem. Gesell., **35**, 1001 (1902).

<sup>3</sup> Proc. Kon. Akad. te Amsterdam, 1903, p. 104.

<sup>4</sup> Ztschr. phys. Chem., **42**, 209 (1903).

<sup>5</sup> *Ibid.*, **40**, 222 (1902).

<sup>6</sup> *Ibid.*, **43**, 257 (1903).

<sup>7</sup> Pogg. Ann., **99**, 229 (1856).

<sup>8</sup> *Ibid.*, **157**, 130 (1876).

Stephan,<sup>1</sup> in 1883, tried a third possibility, by using mixtures of alcohol and water as a solvent. He found that the temperature coefficients of conductivity and of fluidity (the reciprocal of viscosity) closely resembled each other. He observed a minimum in his curves and proposed the formula:

$$\frac{KH}{k\eta} = \text{constant, to hold up to the minimum point,}$$

$$\text{and } \frac{wKH}{w'k\eta} = \text{constant, to hold from that point on;}$$

where  $K$  is the conductivity of the equivalent aqueous solution,  $k$  the conductivity of the mixture, and  $H$  and  $\eta$  the corresponding viscosities;  $w$  and  $w'$  are the per cents of water in the given aqueous mixture and in the aqueous alcoholic mixture of minimal fluidity, respectively. He believed that each ion carries with it neighboring molecules of the solvent, and that ionic friction results from the friction between these and the rest of the solvent.

Dutoit and Friderich<sup>2</sup> introduced the association factor and concluded that—

The values of  $\mu_v$  for a given electrolyte dissolved in different solvents, are a direct function of the degree of polymerization of the solvent and an indirect function of the coefficient of viscosity of these solvents.

A fourth method of changing the fluidity was resorted to by Röntgen,<sup>3</sup> and later by Warburg and Sach,<sup>4</sup> and more exhaustively by Cohen.<sup>5</sup> They subjected the aqueous solution to high pressure. Cohen found that, at low temperatures, the viscosity is decreased by the pressure, but that above 40° the viscosity increases with the pressure. In concentrated solutions of sodium and ammonium chlorides the viscosity increases nearly proportional to the pressure, and nearly independent of the temperature. Hauser<sup>6</sup> showed that, at 32°, the pressure ceased to affect the fluidity of water.

Grossman,<sup>7</sup> in 1883, recalculated Grotrian's results, and found that the conductivity multiplied by the viscosity gave a constant independent of the temperature, and that the temperature coefficients were the same to within 1 per cent.

Arrhenius<sup>8</sup> worked with aqueous solutions to which small amounts of non-electrolytes, such as acetone and methyl and ethyl alcohols, had been added. He pointed out an empirical relation between the conductivity and the fluidity; but he saw that these quantities are not simply dependent on each other, since the conductivities of dilute solutions of different salts are not the same. This empirical relation was further developed by Euler.<sup>9</sup>

<sup>1</sup> Wied. Ann., **17**, 673 (1883).

<sup>2</sup> Bull. Soc. Chim., [3], **19**, 321 (1898).

<sup>3</sup> Wied. Ann., **22**, 510 (1884).

<sup>4</sup> Ibid., **22**, 514 (1884).

<sup>5</sup> Ibid., **45**, 666 (1892).

<sup>6</sup> Ann. d. Phys., **5**, 597 (1901).

<sup>7</sup> Wied. Ann., **18**, 119 (1883).

<sup>8</sup> Ztschr. phys. Chem., **9**, 487 (1892);  
**1**, 285 (1887).

<sup>9</sup> Ibid., **35**, 536 (1898).

We need only mention in this connection the work of Strindberg<sup>1</sup> and of Holland.<sup>2</sup>

Völlmer<sup>3</sup> investigated solutions of various salts in methyl and ethyl alcohols. He found the temperature coefficients of conductivity and fluidity to be very nearly identical.

Kohlrausch and Deguisne<sup>4</sup> used the formula

$$K_t = K_{18}[1 + \alpha(t - 18^\circ) + \beta(t - 18^\circ)^2]$$

to represent the influence of temperature on conductivity, starting from 18° as a mean temperature. Kohlrausch<sup>5</sup> noted that on extrapolating this curve, aqueous solutions would reach a zero value of conductivity at about -39°, which is about the temperature where the fluidity would become zero. Bousfield and Lowry<sup>6</sup> showed that the viscosity of water may be represented accurately by a formula similar to the above,

$$\eta_{18} = \eta_t[1 + \alpha(t - 18) + \beta(t - 18)^2]$$

They found that the constants  $\alpha$  and  $\beta$  are the same in the two formulas, to within the limits of experimental error. They believe, however, that these formulas will not hold at low temperatures, and that the zero values can not be experimentally realized. This belief is borne out by the work of Kunz.<sup>7</sup>

In an exceedingly interesting paper, Kohlrausch<sup>8</sup> proposes the view that—

About every ion there moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion. . . . The electrolytic resistance is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness. . . . For a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, provided the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere becomes, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to observations now at hand, this would seem to be the case for the slowest moving univalent ion, Li.

Bousfield and Lowry<sup>9</sup> have gone farther and have shown that we should also expect to find an upper limit of conductivity, on account of the decrease in dissociation with rise in temperature. A maximum conductivity of this sort has been observed by Franklin and Kraus<sup>10</sup> in liquid ammonia. Potassium iodide gives a maximum in conductivity, in methyl alcohol, at 160°.<sup>11</sup>

<sup>1</sup> Ztschr. phys. Chem., **14**, 221 (1894).

<sup>2</sup> Wied. Ann., **50**, 261 (1892).

<sup>3</sup> Ibid., **52**, 328 (1894).

<sup>4</sup> Dissertation Strassburg, 1893.

<sup>5</sup> Sitz. Berlin. (1901), 1028.

<sup>6</sup> Proc. Roy. Soc., **71**, 42 (1902).

<sup>7</sup> Compt. rend., **135**, 788 (1902).

<sup>8</sup> Proc. Roy. Soc., **71**, 338 (1903).

<sup>9</sup> Loc. cit.

<sup>10</sup> Amer. Chem. Journ., **24**, 83 (1900).

<sup>11</sup> Phys. Rev., **18**, 40 (1904).

Noyes <sup>1</sup> observed a maximum conductivity with N/10 potassium and sodium chlorides, in water, at 280°. The formula of Slotte <sup>2</sup> for variation of fluidity

$$\frac{\eta_0}{\eta} = (1 + bt)^n$$

holds at low temperatures, so that combining this formula with that of Abegg and Seitz for decrease in dielectric constant,

$$\frac{D}{D'} = e^{-at}$$

Bousfield and Lowry <sup>3</sup> give, as the complete formula representing the effect of temperature on conductivity,

$$\frac{K_t}{K_0} = \frac{\rho_v}{\rho_0} (1 + bt)^n e^{-at}$$

Reference should also be made to the work of Hechler.<sup>4</sup>

VISCOSITY.

The majority of workers have confined themselves either to viscosity determinations alone, or to conductivity determinations alone. We must, therefore, consider some of these if we wish to see clearly the relations between the phenomena.

We need simply mention here the work of Poiseuille,<sup>5</sup> Noack,<sup>6</sup> Pagliani and Battelli,<sup>7</sup> Slotte,<sup>8</sup> Gartenmeister,<sup>9</sup> and Traube.<sup>10</sup> The monumental work of Thorpe and Rodger <sup>11</sup> merits more careful attention. They worked with very great accuracy both with pure liquids and with mixtures,<sup>12</sup> and over a considerable range of temperature. They have shown that the formula of Slotte gives the best results. They proved, conclusively, what had been hinted at before, that —

Viscosity may be taken as the sum of the attractive forces in play between the molecules; . . . that an increment of CH<sub>2</sub> in chemical composition, or the substitution of an atom of Cl, Br, or I for an atom of hydrogen, brings about a definite change in the magnitude of the viscosity. It is, therefore, made evident that viscosity or intermolecular attraction is, in reality, a property of the atoms of which the molecules are composed. Isomers have nearly but not the same viscosity, yet the effect of CH<sub>2</sub> is the same as in the normal compounds. The effects due to ring grouping, iso- and double-linkages, and changes in the condition of the oxygen may be quantitatively allowed for. . . . But water and the alcohols show no agreement with the calculated values.

<sup>1</sup> Ztschr. phys. Chem., **46**, 323 (1903).  
 Journ. Amer. Chem. Soc., **26**, 134 (1903).

<sup>2</sup> Beibl., **16**, 182 (1892).

<sup>3</sup> Proc. Roy. Soc., **74**, 280 (1904).

<sup>4</sup> Dissertation Münster (1904).

<sup>5</sup> Mém. Inst. Paris, **9**, 433 (1896).

<sup>6</sup> Wied. Ann., **27**, 289 (1886).

<sup>7</sup> Atti di R. Ac. delle Sc. d. Torino, **20**,  
 607 (1885).

<sup>8</sup> Loc. cit.

<sup>9</sup> Ztschr. phys. Chem., **6**, 524 (1890).

<sup>10</sup> Ber. d. chem. Gesell., **19**, 871 (1886).

<sup>11</sup> Phil. Trans., **185A**, 307 (1894).

<sup>12</sup> Journ. Chem. Soc., **51**, 360 (1897).

Hydrogen is calculated to have an effect on molecular viscosity of 44.5, carbon of 31, and iso-linkage, for example, of -21. The effect is shown in table 3.

TABLE 3. — *Molecular viscosity at slope 0.0000323.*

	Normal compound.		Iso-compound.	
	Found.	Calculated.	Found.	Calculated.
Pentane . . . . .	687	689	663	668
Hexane . . . . .	818	809	799	788
Heptane . . . . .	931	929	908	908
Octane . . . . .	1035	1049	...	...

These investigators found both maxima and minima when working with mixtures, and in the particular case of chloroform and ether they found a point of inflection. They believe that the maximum value is caused by a "feeble chemical combination or molecular aggregation, which is destroyed by heat or dilution."

It is to be expected that water and the alcohols would give abnormal results, since Ramsay and Shields<sup>1</sup> have shown that these liquids are associated. They are also abnormal in possessing a high dielectric constant.<sup>2</sup> Some of the characteristic properties of water, methyl alcohol, ethyl alcohol, and acetone are grouped together in table 4.

TABLE 4.

	Mol. vol.	Viscosity.	Association.	Dielectric constant.
Water . . . . .	{ 18.0 at 0°	0.01778 at 0°	1.707 at 0°	79.46 at 0°
	{ 18.1 25			
Methyl alcohol . .	{ 39.5 0	.0080846 0	2.65 - 90	34.05
	{ 40.3 20			
Ethyl alcohol . . .	{ 57.1 0	.017761 0	2.03 - 90	25.02
	{ 58.3 20			
Acetone . . . . .	{ 70.9 0	.0039496 0	1.26 17 to 78	21.85
	{ 73.2 20			

No such quantitative relation has been worked out for changes in viscosity caused by salts brought into solution, and still less is known about the conductivity which a given salt may be expected to give. Yet Bredig,<sup>3</sup> Wagner,<sup>4</sup> and Euler<sup>5</sup> have worked on this problem with considerable success. Wagner found that the viscosity of a salt solution is an additive function of the metallic and non-metallic radicals of the dissolved salt. For allied metals the viscosity decreases as the atomic weight increases. The dissociated ions appear in

<sup>1</sup> Ztschr. phys. Chem., **12**, 433 (1893);  
**15**, 111 (1894).  
 Ibid., **14**, 286 (1894).

<sup>3</sup> Ibid., **13**, 243 (1894).  
<sup>4</sup> Ibid., **5**, 31 (1890).  
<sup>5</sup> Ibid., **25**, 536 (1898).

some cases to have greater, and in other cases less viscosity than the original solution.

To explain this "negative viscosity" shown by certain salts in their power to lower the viscosity of pure water, Euler employed the "electrostriction theory" proposed by Drude and Nernst.<sup>1</sup> According to this theory the ion is surrounded by a strong electrical field, in virtue of its charge, which causes a strong compression of the liquid in this field. Euler holds that the effect of a salt on viscosity is the result of two tendencies: First, that of the atoms tending to increase the viscosity in inverse proportion to their migration velocities; and second, the electrostriction tending to lessen the viscosity.

Euler has calculated viscosity constants for a large number of ions, and finds the relation between them and the migration velocities to be expressed by the formula —

$$(A - 0.68) \cdot U \text{ (or } (K - 0.68) \cdot V) = \text{a constant,}$$

where *A* and *K* are the viscosity constants and *U* and *V* are the migration velocities of the anion and cation, respectively. Hydrogen and hydroxyl ions are exceptions. Some of the values are given in table 5.

TABLE 5.

Ion.	Migration velocity.	Viscosity constant.
Li . . . . .	39.8	1.15
Ca . . . . .	62.0	1.023
K . . . . .	70.6	0.962
Br . . . . .	73.0	0.946
NO <sub>3</sub> . . . . .	....	0.919

Wagner<sup>2</sup> has shown that Mullenbein's<sup>3</sup> measurements have discounted Euler's explanation of negative viscosity, since the viscosity of the solvent may be lowered by the addition of certain non-electrolytes, even when the viscosity of the dissolved substance is higher than that of the solvent. With ethyl alcohol, *o*-nitrotoluene gives an inversion-point, *m*-nitrotoluene a minimum and *p*-nitrotoluene a maximum.

He proposes, as an explanation, that the solute diminishes the quantity of the solvent in a given space, and this leads to a diminution of the viscosity, which diminution is partly compensated, however, by the solute itself. According to the relative magnitude of the various factors, the viscosity may be increased or diminished.

Dunstan<sup>4</sup> has investigated a large number of mixtures. He believes that the increase in viscosity is due to the formation of loosely held complexes.

<sup>1</sup> Ztschr. phys. Chem., **15**, 79 (1894).

<sup>2</sup> Ibid., **46**, 867 (1903).

<sup>3</sup> Dissertation, Leipzig, 1901.

<sup>4</sup> Journ. Chem. Soc., **85**, 817 (1904). Ztschr. phys. Chem., **49**, 590 (1904).

He thinks that the cause of the minimum in viscosity is more deep-seated than Wagner supposed, and attributes it to "some change in molecular aggregation or dissociation."

Blanchard<sup>1</sup> found that the addition of 1 equivalent of ammonia for 1 equivalent of silver, and the addition of 4 equivalents of ammonia for 1 equivalent of copper and zinc in aqueous solutions of their salts, very greatly decreases the viscosity. He reasons that this can not be due to increased ionization, and therefore rejects the electrostriction theory and proposes a hydrate theory. He says that if the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules can not decrease its mass or readily increase its symmetry, so as to reduce the viscosity. The only explanation seems to be that the ions in solution are hydrated. The hydrate water is replaced by ammonia, which forms with the ion a more stable complex and one of smaller mass, or greater symmetry, or both. He believes that this theory also accounts for negative viscosity and for the effect of pressure on viscosity. Evidently, this is the same conclusion as that reached by Kohlrausch in his hypothesis of ionic spheres, but by a somewhat different method of approach.

Blanchard added small amounts of water to alcoholic solutions of sodium hydroxide, and found the viscosity smaller than would be expected from a study of the pure solvents. This is due, as he thinks, to the formation of a complex between the alkali, water, and alcohol, which is, however, smaller or more symmetrical than the alcohol-water complex originally present. Mixtures of alcohol and water give a maximum in viscosity. Blanchard finds that cupric chloride increases this effect. He further applies this theory to the work of Jones and Lindsay,<sup>2</sup> on conductivity.

The existence of hydrates, or solvates (in the case of non-aqueous solvents) in one form or another is an old conception. Pousseuille<sup>3</sup> first suggested it in working with alcohol and water. Graham<sup>4</sup> confirmed and extended Pousseuille's work. Wijkander<sup>5</sup> supposed that acetic acid forms a hydrate with water,  $C_2H_4O_2 \cdot H_2O$ , which would account for abnormal viscosity. The changes due to temperature he attributed to dissociation changes in the liquid. Thorpe and Rodger<sup>6</sup> and Traube<sup>6</sup> also assume the presence of hydrates.

Recently, Varenne and Godefroy<sup>7</sup> have found evidence from viscosity curves for the existence of various hydrates in mixtures of water with methyl and ethyl alcohols and acetone. These are shown in table 6.

<sup>1</sup> Journ. Amer. Chem. Soc., **26**, 1315 (1904).

<sup>2</sup> Amer. Chem. Journ., **28**, 329 (1902).

<sup>3</sup> Loc. cit.

<sup>4</sup> Phil. Trans., **151**, 373 (1861).

<sup>5</sup> Wied. Beibl., **8**, 3 (1879).

<sup>6</sup> Loc. cit.

<sup>7</sup> Compt. rend., **137**, 992 (1903); **138**, 990 (1904).



TABLE 6.

Methyl alcohol and water.	Ethyl alcohol and water.	Acetone and water.
CH <sub>3</sub> OH . H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH . 2 H <sub>2</sub> O	CH <sub>3</sub> COCH <sub>3</sub> . 3 H <sub>2</sub> O
CH <sub>3</sub> OH . 2 H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH . 3 H <sub>2</sub> O	CH <sub>3</sub> COCH <sub>3</sub> . 4 H <sub>2</sub> O
CH <sub>3</sub> OH . 3 H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH . 6 H <sub>2</sub> O	CH <sub>3</sub> COCH <sub>3</sub> . 8 H <sub>2</sub> O
CH <sub>3</sub> OH . 5 H <sub>2</sub> O	3 (C <sub>2</sub> H <sub>5</sub> OH) . 2 H <sub>2</sub> O	CH <sub>3</sub> COCH <sub>3</sub> . 34 H <sub>2</sub> O
CH <sub>3</sub> OH . 8 H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH . 22 H <sub>2</sub> O	
CH <sub>3</sub> OH . 20 H <sub>2</sub> O		

This conception of the existence of hydrates differs from the view put forward by Jones,<sup>1</sup> according to which the composition of the hydrates formed by any substance is a function of the concentration, the temperature remaining constant. The composition may vary all the way from one molecule of water to a large number, every intermediate step being represented. Various lines of evidence have been furnished for this view by Jones,<sup>2</sup> Jones and Getman,<sup>3</sup> Jones and Bassett,<sup>4</sup> and Jones and Uhler.<sup>5</sup> The more important of these have to do with the relation between water of crystallization and lowering of the freezing-point, dissociation as measured by freezing-point and by conductivity, certain color changes in solution, and the relation between water of crystallization and temperature.

<sup>1</sup> Amer. Chem. Journ., **23**, 89 (1900).

<sup>2</sup> Loc. cit.

<sup>3</sup> Amer. Chem. Journ., **31**, 303 (1904). Ztschr. phys. Chem., **46**, 244 (1903); **49**, 385 (1904).

<sup>4</sup> Amer. Chem. Journ., **33**, 584 (1905).

<sup>5</sup> Carnegie Institution of Washington Publication No. 60. Amer. Chem. Journ., **37**, 126 (1907).

## WORK OF LINDSAY.

### EXPERIMENTAL.

This work was undertaken as an extension of the older work of Zelinsky and Krapiwín,<sup>1</sup> and Cohen,<sup>1</sup> on the conductivity of electrolytes in mixtures of methyl and ethyl alcohols with water. Zelinsky and Krapiwín, in their work, have shown that solutions in a 50 per cent mixture of methyl alcohol and water have a much less conductivity than in the pure alcohol itself. They have also shown that the slightest addition of water to a solution of an electrolyte in absolute methyl alcohol produced a lowering of its conducting power.

We have extended this work, by making conductivity measurements of solutions in which the solvents were mixtures of methyl alcohol and water of varying composition. By this means we have been able to plot curves showing, for each salt worked with, the mixture of methyl alcohol and water having the least dissociating power. We have also extended the investigation to ethyl alcohol, propyl alcohol, and to mixtures of ethyl alcohol and water, propyl alcohol and water, and methyl and ethyl alcohols.

The work has, for the most part, been done both at 0° and 25°. In this way we have been able to calculate the temperature coefficients of conductivity of the various salts in the different solvents and, what is of more importance, to show the influence of temperature on the minimum values mentioned above. The salts used are potassium iodide, strontium iodide, ammonium bromide, cadmium bromide, ferric chloride, and lithium nitrate.

### APPARATUS.

In all this work the Kohlrausch method of measuring conductivity was employed. The bridge wire used was a meter in length and made of "manganin." The resistance coils were manufactured by Leeds & Co., of Philadelphia, and were found to be accurate to 0.04 per cent.

The cells are of the form shown in fig. 1, the difference between them and the ordinary Arrhenius cell being that they are provided with a ground-glass top to prevent evaporation of the more volatile solvents, and to protect the anhydrous alcohols from the moisture of the baths and air. In some cases the ground-glass joint was also covered with paraffin as an extra precaution.

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<sup>1</sup> Loc. cit.

The glass tubes carrying the electrodes were shoved through thin rubber tubes, and then inserted into the glass tubes in the cap. Sealing wax was then run over the outside of the joint.

The zero-bath was prepared as follows: A large glass battery-jar was filled with pure, finely crushed ice, and moistened with distilled water. This was placed in a water-bath, the space between the two being filled with finely crushed ice. By this means it was possible to keep a cell within  $0.02^\circ$  of zero for hours. The  $25^\circ$  bath was of the ordinary form and was stirred by means of a small hot-air engine.

The thermometers used were graduated to  $0.04^\circ$  and were carefully calibrated. The burettes and flasks were also carefully calibrated.

#### SOLVENTS.

##### WATER.

All the water used in this work was purified as follows: Ordinary distilled water was first distilled from acidified potassium dichromate. This water was redistilled from potassium dichromate acidified with sulphuric acid, and then from barium hydroxide. The water purified in this way had a conductivity of never more than  $2 \times 10^{-6}$ , and sometimes as low as  $0.8 \times 10^{-6}$ .

##### METHYL ALCOHOL.

The methyl alcohol used was the best commercial article that could be obtained. It was first boiled with calcium oxide, then distilled and allowed to stand over anhydrous copper sulphate for weeks. Before use it was distilled from the copper sulphate and then from sodium. None of the alcohol used in making up the solutions in absolute alcohol had been distilled from sodium more than twenty-four hours before use. It had a conductivity of about  $2.3 \times 10^{-6}$ .

##### ETHYL ALCOHOL.

The ethyl alcohol was the best obtainable article, and was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of  $2 \times 10^{-7}$ .

##### PROPYL ALCOHOL.

The propyl alcohol was Kahlbaum's best, and before use was distilled from anhydrous copper sulphate and sodium. It had a conductivity of  $0.8 \times 10^{-7}$ .

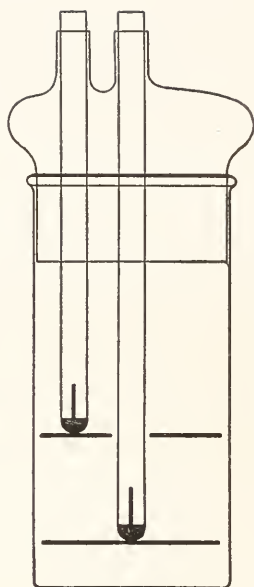


FIG. 1.

## SOLUTIONS.

The method of making up the original mother-solutions will be given when the various electrolytes are considered. From this mother-solution the remaining solutions were made by successive dilutions by means of burettes and measuring flasks. In the cases where this would necessitate the use of small quantities of the solution, a second mother-solution was made, and from this successive dilutions were prepared.

In preparing the solutions in the mixed solvents, a sufficient quantity of the solvent was made by mixing the constituents in the required proportions. This was then used in the same manner as a simple solvent. In preparing these mixed solvents the following method was employed:  $x$  c.c. of an alcohol were diluted to 100 c.c. In the following discussion such a solution would be designated as — alcohol  $x$  per cent. In making mixtures of methyl alcohol and ethyl alcohol, the methyl alcohol was measured and diluted with the ethyl alcohol, and the concentration expressed in terms of the methyl alcohol.

## CONDUCTIVITY MEASUREMENTS.

In all determinations of conductivity from three to five different resistances were used, and the values given in the tables are the mean of these values.

## POTASSIUM IODIDE.

The salt used in this work was recrystallized a number of times. It was then carefully dried and kept in a desiccator. All the mother-solutions were made by direct weighing.

TABLE 7. — *Molecular conductivity of potassium iodide.*

$v$	In water.		In methyl alcohol.		In ethyl alcohol.	
	$^1 \mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
64	74.09	132.1	59.32	82.87	19.12	29.40
128	76.4 D	135.4	63.88	88.49	21.36	33.02
256	77.01	138.0	67.73	93.73	22.66	36.02
512	78.0 D	139.6	69.85	98.36	25.00	38.63
1024	77.96	140.7	71.23	102.0	27.43	41.35

$v$	In methyl alcohol.		In methyl alcohol (20 p. ct.) and water.		In methyl alcohol (40 p. ct.) and water.		In methyl alcohol (50 p. ct.) and water.	
	$^1 \mu_v 25^\circ$	$^2 \mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
64	78.7	82.52	45.69	91.91	35.48	72.14	33.73	67.46
128	84.7	88.69	47.26	93.78	35.92	73.69	34.44	68.79
256	88.2	93.85	47.79	95.64	36.52	75.14	35.13	70.37
512	90.8	98.19	48.45	97.12	37.02	76.25	36.05	71.72
1024	93.0	102.2	49.07	98.10	37.85	77.68	36.76	72.57

<sup>1</sup> The values of the conductivity at  $0^\circ$  marked "D" were obtained by Jones and Douglas (Amer. Chem. Journ., 26, 428), while those at  $25^\circ$  are taken from the work of Ostwald.

<sup>2</sup> Carrara.

<sup>3</sup> Zelinsky and Krapiwlin.

TABLE 7.—*Molecular conductivity of potassium iodide.*—Continued.

<i>v</i>	In methyl alcohol (65 p. ct.) and water.		In methyl alcohol (80 p. ct.) and water.		In ethyl alcohol (50 p. ct.) and water.		In methyl alcohol (50 p. ct.) and ethyl alcohol.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
64	35.12	65.04	39.03	67.78	19.26	48.30	36.74	54.18
128	35.71	67.25	40.51	70.33	19.82	50.07	39.46	58.52
256	36.49	68.78	41.83	71.83	20.35	50.80	41.93	62.13
512	37.23	70.00	43.23	73.16	20.92	51.97	44.46	65.93
1024	37.75	70.94	44.45	74.81	21.43	52.52	46.89	69.61

The conductivity of solutions of potassium iodide in methyl alcohol had already been determined by both Zelinsky and Krapiwini,<sup>1</sup> and Carrara,<sup>2</sup> but with such different results that the above measurements seemed necessary. Our measurements agree very well with those of Zelinsky and Krapiwini, as is seen from table 7.

TABLE 8.—*Temperature coefficients of conductivity of potassium iodide.*

<i>v</i>	In water (0° to 25°).		In methyl alcohol (0° to 25°).			In ethyl alcohol (0° to 25°).	
64	2.26		0.942			0.411	
128	2.30		0.984			.466	
256	2.35		1.04			.534	
512	2.40		1.14			.545	
1024	2.52		1.23			.557	

<i>v</i>	In mixtures of methyl alcohol and water of various compositions.					In a 50 p. ct. mixture of ethyl alcohol and water (0° to 25°).	In a 50 p. ct. mixture of methyl and ethyl alcohols (0° to 25°).
	20 p. ct.	40 p. ct.	50 p. ct.	65 p. ct.	80 p. ct.		
64	1.83	1.47	1.35	1.17	1.15	1.16	0.698
128	1.86	1.51	1.37	1.26	1.17	1.25	.762
256	1.91	1.54	1.41	1.29	1.20	1.22	.808
512	1.95	1.57	1.43	1.31	1.20	1.24	.859
1024	1.96	1.59	1.43	1.32	1.21	1.24	.909

Some of the results given in table 7 are plotted in fig. 3. The curves are of the same general form as the preceding. The chief points of difference are: The minimum point has shifted to the right, corresponding now to an alcohol-water mixture of about 65 per cent. The increase to the right of the minimum is much less rapid than that to the left, the difference being due to the fact that the temperature coefficient of conductivity is much greater in water than in methyl alcohol. The alcohol-water mixture, having the same conducting power as the solution in pure methyl alcohol, has also changed. In this case it changes from an alcohol of about 19 per cent to an alcohol of about 30 per cent, depending upon the concentration of the solution.

<sup>1</sup> Ztschr. phys. Chem., **21**, 35 (1896).

<sup>2</sup> Gazz. Chim. Ital., **26**, (1) 119 (1896).

TABLE 9. — Comparison of the molecular conductivity of potassium iodide.

$\nu$	In ethyl alcohol, water, and a 50 p. ct. mixture of these solvents.					
	At 0°.			At 25°.		
	Water. $\mu_v$	Mixture. $\mu_v$	Ethyl alcohol. $\mu_v$	Water. $\mu_v$	Mixture. $\mu_v$	Ethyl alcohol. $\mu_v$
64	74.09	19.26	19.12	132.1	48.30	29.40
128	76.4	19.82	21.36	135.4	50.07	33.02
256	77.01	20.35	22.66	138.0	50.80	36.02
512	78.0	20.92	25.00	139.6	51.97	38.63
1024	77.96	21.43	27.43	140.7	52.52	41.35

$\nu$	In water, methyl alcohol, and mixtures of these solvents at 0°.						
	0 p. ct.	20 p. ct.	40 p. ct.	50 p. ct.	65 p. ct.	80 p. ct.	100 p. ct.
64	74.09	....	35.48	33.73	35.12	39.03	59.32
128	76.4 D	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.83	67.73
512	78.0 D	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.96	49.07	37.85	36.76	37.75	44.45	71.23

$\nu$	In water, methyl alcohol, and mixtures of these solvents at 25°.						
	0 p. ct.	20 p. ct.	40 p. ct.	50 p. ct.	65 p. ct.	80 p. ct.	100 p. ct.
64	132.1	91.91	72.14	67.46	65.04	67.78	82.87
128	135.4	93.78	73.69	68.79	67.25	70.33	88.49
256	138.0	95.64	75.14	70.37	68.78	71.83	93.73
512	139.6	97.12	76.25	71.72	70.00	73.16	98.00
1024	140.7	98.10	77.68	72.57	70.94	74.81	102.0

$\nu$	In methyl alcohol, ethyl alcohol, and a 50 p. ct. mixture of these solvents.					
	At 0°.			At 25°.		
	Methyl alcohol. $\mu_v$	Mixture. $\mu_v$	Ethyl alcohol. $\mu_v$	Methyl alcohol. $\mu_v$	Mixture. $\mu_v$	Ethyl alcohol. $\mu_v$
64	59.32	36.74	19.12	82.87	54.18	29.40
128	63.88	39.46	21.36	88.49	58.52	33.02
256	67.73	41.93	22.66	93.73	62.13	36.02
512	69.85	44.46	25.00	98.36	65.93	38.63
1024	71.23	46.89	27.43	102.0	69.61	41.35

Cohen<sup>1</sup> has shown that solutions of potassium iodide in a mixture of alcohol and water show a minimum in the conductivity, but only at great dilutions (512) and when the amount of water present is small. His work, however, was all done at 18° C. From the results in table 9 we see that at 0° we have a minimum in the conductivity values for an alcohol as dilute as 50 per cent, and in solutions which are comparatively strong, namely, from  $\nu = 128$ . In all probability in alcohol of 75 to 80 per cent a much greater depression

<sup>1</sup> Ztschr. phys. Chem., 25, 31 (1898).

would be found. This is, however, a subject for future investigation. At 25° all trace of a minimum has disappeared.

In order to see the connection existing between the conducting power of the solutions in the various solvents, the preceding table is given for the sake of comparison.

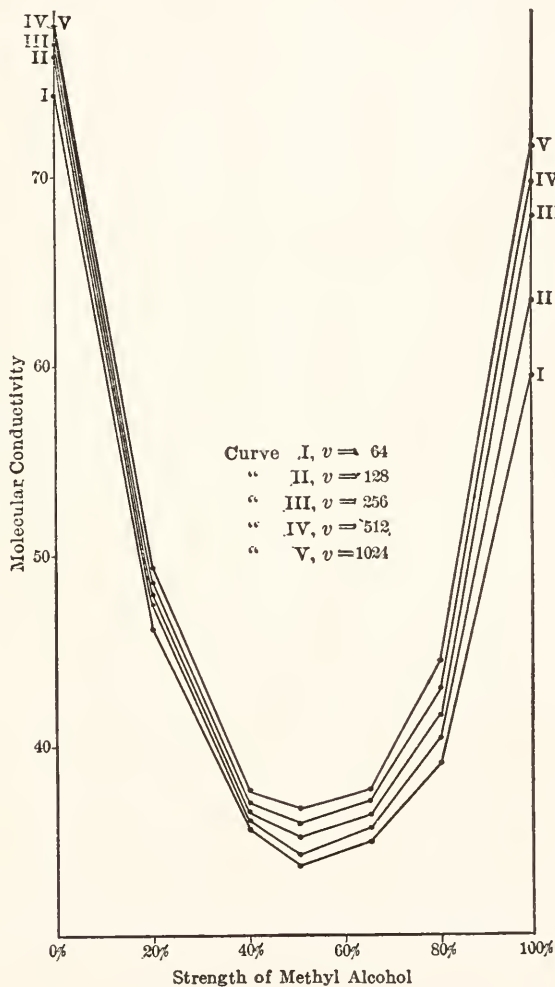


FIG. 2.— POTASSIUM IODIDE AT 0°.

Some of the values in table 9 are plotted in fig. 2. It is seen that the values of the molecular conductivity reach a minimum in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol. It is also seen that an addition of approximately 10 per cent of alcohol lowers the conductivity of the aqueous solutions to that of an alcoholic solution.

Table 9 makes it clear that in a mixture of methyl and ethyl alcohols, the conductivity of potassium iodide shows no minimum value when compared with the conductivity in the pure solvents. In fact, the conductivity values

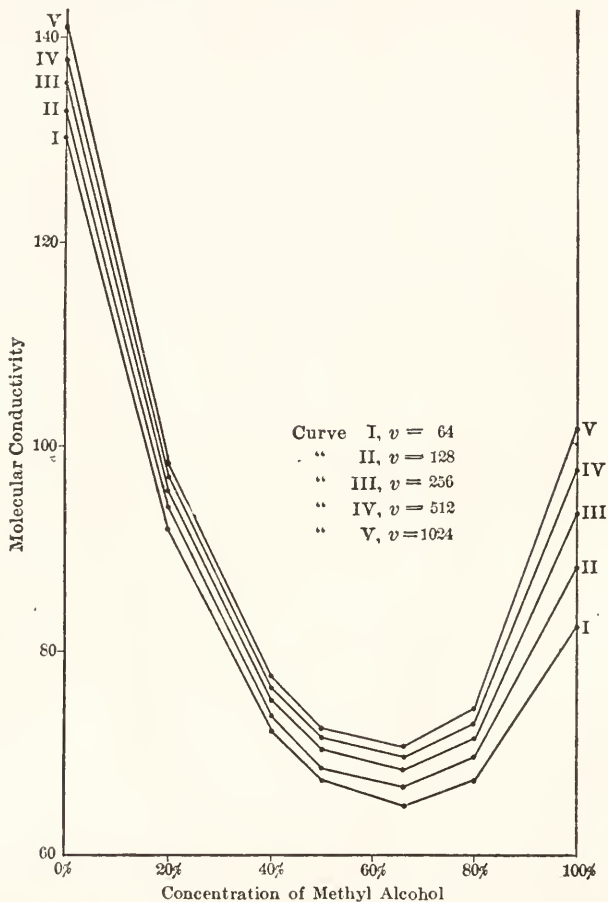


FIG. 3. — POTASSIUM IODIDE AT 25°.

for the solutions in the mixed solvents approach the mean value of the conductivities in the pure solvents. Thus, at 0° the observed value of the conductivity in the mixture, for  $v=64$ , is 36.74, while the mean of the conductivities at the same dilution in the pure solvents is 39.22. In all cases, however, the conductivity in the mixture lies below this mean value.

#### AMMONIUM BROMIDE.

The salt used in this work was carefully recrystallized, and on sublimation left no residue. It was thoroughly dried and kept in a desiccator. All the mother-solutions were made by direct weighing.



TABLE 10. — *Molecular conductivity of ammonium bromide.*

$v$	In water.		In methyl alcohol.		In ethyl alcohol.
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$
64	74.22	135.3	58.71	79.56	16.71
128	75.23	138.6	63.16	85.80	18.83
256	76.62	141.2	66.45	90.88	19.66
512	77.49	143.5	68.51	94.99	22.66
1024	77.78	145.6	70.40	98.24	22.88

$v$	In methyl alcohol (50 p. ct.) and water.	In ethyl alcohol (50 p. ct.) and water.	In methyl alcohol (50 p. ct.) and ethyl alcohol.	In methyl alcohol, water, and mixtures of these solvents at $0^\circ$ ( $v=64$ ).	
	$\mu_v 0^\circ$	$\mu_v 0^\circ$	$\mu_v 0^\circ$	Alcohol, p. ct.	$\mu_v 0^\circ$
64	34.85	19.42	34.15	0	74.22
128	35.78	19.89	38.40	20	47.96
256	36.36	20.09	39.75	50	34.85
512	37.11	20.70	41.06	65	34.68
1024	37.49	21.50	42.00	80	40.55
				100	58.71

We see that in these results we have practically the same phenomenon as in the case of potassium iodide. In the case of ammonium bromide the minimum point in the conductivity values appears to be reached with an alcohol of 50 per cent.

TABLE 11. — *Temperature coefficients of conductivity of ammonium bromide.*

$v$	In water ( $0^\circ$ to $25^\circ$ ).	In methyl alcohol ( $0^\circ$ to $25^\circ$ ).
64	2.44	0.834
128	2.54	0.906
256	2.58	0.977
512	2.64	1.059
1024	2.71	1.114

TABLE 12. — *Comparison of the molecular conductivity of ammonium bromide.*

$v$	In water, methyl alcohol, and a 50 p. ct. mixture of these solvents at $0^\circ$ .			<sup>1</sup> In water, ethyl alcohol, and a 50 p. ct. mixture of these solvents at $0^\circ$ .			<sup>2</sup> In methyl alcohol, ethyl alcohol, and a 50 p. ct. mixture of these solvents at $0^\circ$ .		
	Water. $\mu_v 0^\circ$	Mixture. $\mu_v 0^\circ$	Methyl alcohol. $\mu_v 0^\circ$	Water. $\mu_v 0^\circ$	Mixture. $\mu_v 0^\circ$	Ethyl alcohol. $\mu_v 0^\circ$	Methyl alcohol. $\mu_v 0^\circ$	Mixture. $\mu_v 0^\circ$	Ethyl alcohol. $\mu_v 0^\circ$
64	74.32	34.85	58.71	74.22	19.42	16.71	58.71	34.15	16.71
128	75.23	35.78	63.16	75.23	19.89	18.83	63.16	38.40	18.83
256	76.62	36.36	66.45	76.62	20.09	19.66	66.45	39.75	19.66
512	77.49	37.11	68.51	77.49	20.70	22.66	68.51	41.06	22.66
1024	77.78	37.49	70.40	...	21.50	22.88	70.40	42.00	22.88

<sup>1</sup> Here also a 50 per cent ethyl alcohol gives a minimum, but only in the case of the more dilute solutions, namely, for dilutions  $v=512$  and  $1024$ .

<sup>2</sup> In this comparison there is no trace of a minimum, nor does there appear to be a probability of a minimum for any mixture of methyl and ethyl alcohols.

## STRONTIUM IODIDE.

The strontium iodide used in this work was a sample of Bender and Hohein's best material. It was freed from all impurities. The material was dried as follows: It was carefully heated with a little ammonium iodide in a current of pure, dry hydrogen, until all the water and ammonium iodide had been driven off. After cooling in the stream of hydrogen it was at once dissolved. The solutions were perfectly neutral and showed not the slightest coloration with a starch solution. No trace of ammonium salts could be detected. The solutions were preserved in the dark in tightly stoppered bottles.

TABLE 13.—*Molecular conductivity of strontium iodide.*

$\nu$	In water.		In methyl alcohol.		In ethyl alcohol.		In propyl alcohol.	
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$
32	113.1	205.3	75.82	101.4	17.44	24.00	4.70	7.58
64	117.7	214.5	85.01	115.3	20.28	28.88	5.62	8.84
128	122.1	223.1	94.76	128.6	23.66	33.53	6.52	10.20
256	126.0	231.8	104.4	141.4	27.00	38.88	7.41	11.32
512	129.8	240.2	114.0	153.9	32.07	46.13	....	....
1024	132.6	245.9	123.4	166.3	36.01	51.25	....	....

$\nu$	In methyl alcohol (25 p. ct.) and water.		In methyl alcohol (50 p. ct.) and water.		In methyl alcohol (75 p. ct.) and water.		In ethyl alcohol (50 p. ct.) and water.		In propyl alcohol (50 p. ct.) and water.	
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$
32	63.06	131.3	50.19	103.8	55.53	98.09	28.32	72.51	27.40	67.67
64	66.05	138.5	52.61	109.9	59.24	104.8	29.72	76.89	28.63	71.63
128	68.62	145.3	55.05	115.3	62.85	111.4	31.25	80.21	29.83	75.44
256	70.98	152.3	57.18	120.1	66.68	118.0	32.23	83.21	30.98	79.32
512	73.10	157.4	....	124.3	69.98	124.8	33.22	86.44	....	....
1024	75.51	161.9	61.03	128.5	73.22	131.4	34.16	89.32	....	....

TABLE 14.—*Temperature coefficients of conductivity of strontium iodide.*

$\nu$	In water (0° to 25°).	In methyl alcohol (0° to 25°).	In ethyl alcohol (0° to 25°).	In propyl alcohol (0° to 25°).	In ethyl alcohol (50 p. ct.) and water (0° to 25°).	In propyl alcohol (50 p. ct.) and water (0° to 25°).	In various mixtures of methyl alcohol and water.		
							25 p. ct.	50 p. ct.	75 p. ct.
32	3.29	1.02	0.262	0.115	1.77	1.61	2.73	2.14	1.70
64	3.87	1.21	.344	.129	1.89	1.72	2.90	2.29	1.82
128	4.04	1.35	.396	.147	1.96	1.82	3.07	2.41	1.94
256	4.23	1.48	.475	.156	2.04	1.93	3.25	2.52	2.05
512	4.42	1.60	.562	....	2.13	....	3.37	2.59	2.19
1024	4.53	1.72	.610	....	2.21	....	3.45	2.70	2.33

Some of the results in table 13 are plotted in fig. 4. It is seen that the curve is of the same form as that for potassium iodide at the same temperature. The minimum point is reached with an alcohol of about 50 per cent.

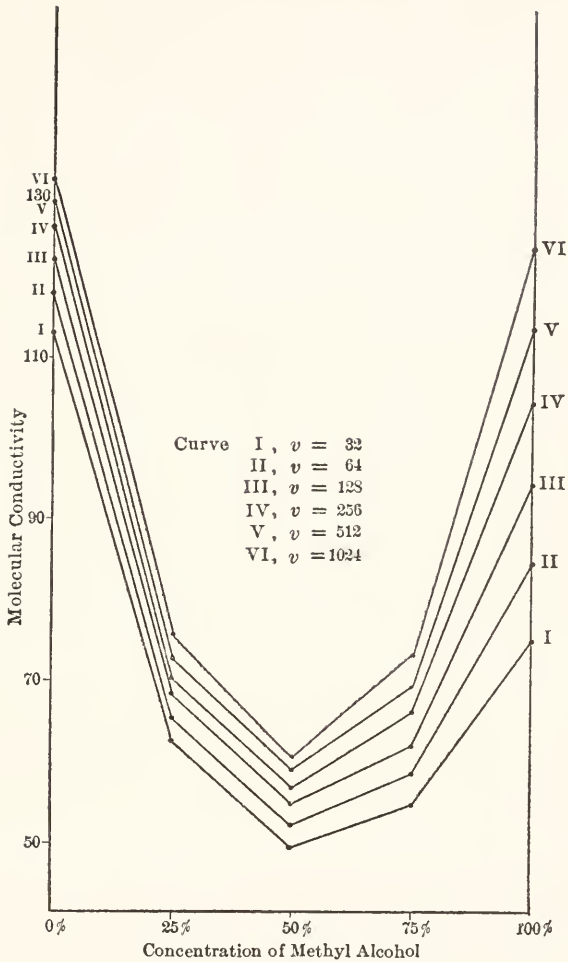


FIG. 4. — STRONTIUM IODIDE AT 0°.

TABLE 15. — Comparison of the molecular conductivity of strontium iodide.

$v$	In water, methyl alcohol, and mixtures of these solvents.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
32	113.1	63.06	50.19	55.53	75.82	205.3	131.3	103.8	98.09	101.4
64	117.7	66.05	52.61	59.24	85.01	214.5	138.5	109.9	104.8	115.3
128	122.1	68.62	55.05	62.85	94.76	223.1	145.3	115.3	111.4	128.6
256	126.0	70.98	57.18	66.68	104.4	231.8	152.3	120.1	118.0	141.4
512	129.8	73.10	59.51	69.98	114.0	240.2	157.4	124.3	124.8	153.9
1024	132.6	75.51	61.03	73.22	123.4	245.9	161.9	128.5	131.4	166.3

TABLE 15.—*Comparison of the molecular conductivity of strontium iodide.*—Continued.

<i>v</i>	In water, ethyl alcohol, and a 50 p. ct. mixture of these solvents.					
	At 0°.			At 25°.		
	Water. $\mu_v$	Mixture. $\mu_v$	Ethyl alcohol. $\mu_v$	Water. $\mu_v$	Mixture. $\mu_v$	Ethyl alcohol. $\mu_v$
32	113.1	28.32	17.44	205.3	72.51	24.00
64	117.7	29.72	20.28	214.5	76.89	28.88
128	122.1	31.25	23.66	223.1	80.21	33.53
256	126.0	32.23	27.00	231.8	83.21	38.88
512	129.8	33.22	32.07	240.2	86.44	46.13
1024	132.6	34.16	36.01	245.9	89.32	51.25

Some of the results in table 15 are plotted as fig. 5. It is seen that in this curve the effect of temperature has been such as almost to blot out the minimum value in the curve for  $v=32$ ; and in the other dilutions the minimum is much less pronounced than in the curves thus far studied. The effect of temperature is also to shift the minimum point to the right, the minimum point existing for an alcohol of about 65 to 70 per cent.

In table 15 for 0° we see that the values for pure ethyl alcohol are, in the stronger solutions, much smaller than those for the mixture. They, however, increase more rapidly, and in the most dilute solutions pass the values for the mixture, giving us again the minimum point. At 25° there is not the slightest trace of a minimum point, although the values are well below the mean of the values for the pure solvents.

In comparing the values for a mixture of propyl alcohol and water with those for the pure solvents, we find that there is not the slightest trace of a minimum either at 0° or 25°.

#### CADMIUM IODIDE.

The cadmium iodide which was used was a sample which had been employed in some previous work in this laboratory, and had then been very carefully purified. The solutions were made by direct weighing.

TABLE 16.—*Comparison of the molecular conductivity of cadmium iodide.*

<i>v</i>	In methyl alcohol, water, and a 50 p. ct. mixture of these solvents at 25°.			In varying mixtures of methyl alcohol and water at 25°.		
	Water. $\mu_v$	Mixture. $\mu_v$	Methyl alcohol. $\mu_v$	Concentration of alcohol, p. ct.	$v=16$ . $\mu_v$	$v=64$ . $\mu_v$
16	62.98	20.31	13.07	0	62.98	104.7
32	81.96	24.22	13.59	50	20.31	31.17
64	104.7	31.17	14.16	60	...	25.66
128	129.3	42.03	14.78	80	14.70	18.41
256	153.6	50.43	15.44	100	13.07	14.16

When the results in the second part of table 16 are plotted as curves, no trace of a minimum appears (fig. 6). A considerable difference, however, is noticed between the values obtained and those required from the law of mixtures, the conductivity values obtained being always lower.

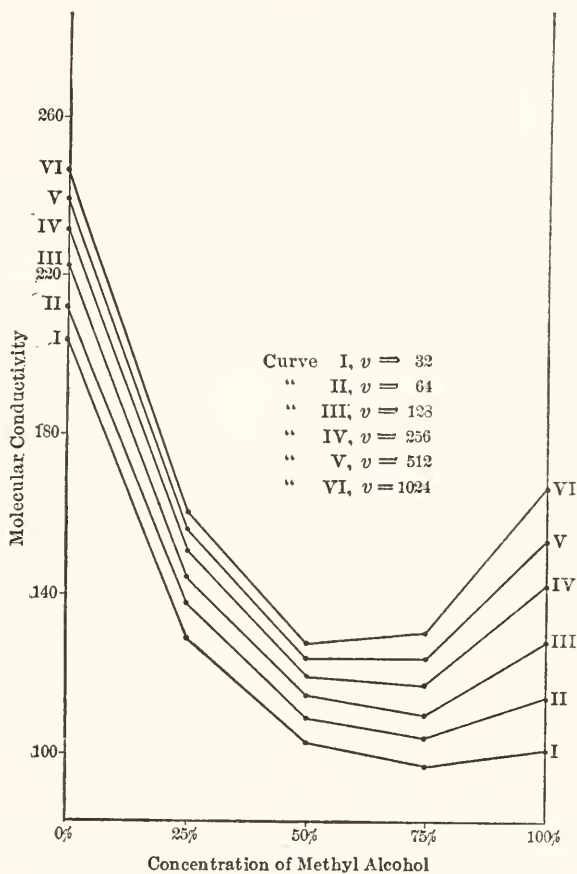


FIG. 5.—STRONTIUM IODIDE AT 25°.

#### LITHIUM NITRATE.

The lithium nitrate used in this work was a sample obtained from Kahlbaum. It was dried in an air-bath at 150° and kept in a desiccator. The solutions were made by direct weighing.

From table 17 we see that at 0° the conductivity in pure methyl alcohol, although starting lower than the conductivity in water, increases more rapidly, so that we have solutions in methyl alcohol with greater conductivity than

solutions of the same strength in water. That our measurements are fairly accurate is made more probable by the close agreement with the values obtained by Ostwald. The solutions measured at  $0^\circ$  were the same as at  $25^\circ$ . The conductivity of a number of the solutions in methyl alcohol was redetermined, using a different sample of the alcohol and salt. In all cases the agreement was all that could be desired.

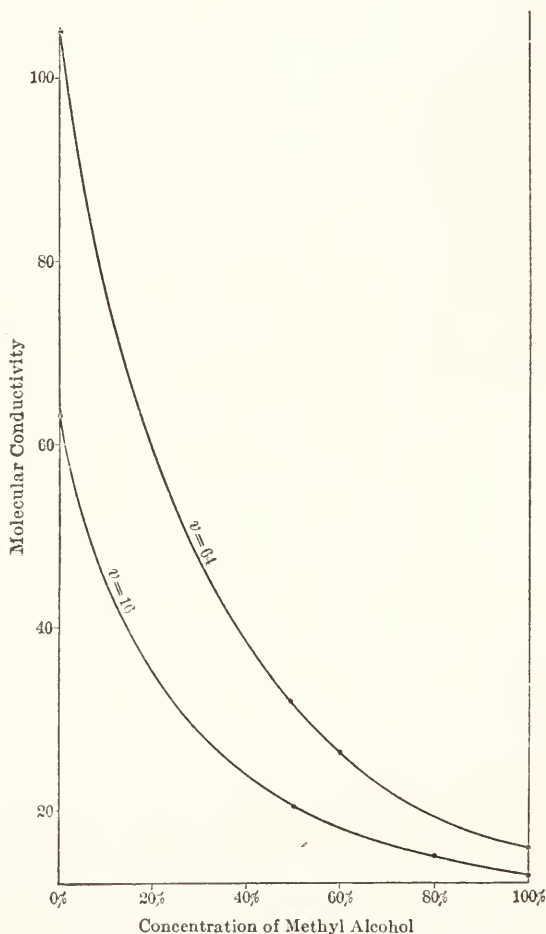


FIG. 6.—CADMIUM IODIDE.

From table 17 it is seen that with lithium nitrate in ethyl alcohol a minimum point is found in the conductivity values at  $0^\circ$ , and through all the dilutions employed. At  $25^\circ$  no trace of minimum values is apparent.

TABLE 17. — *Molecular conductivity of lithium nitrate.*

$\nu$	In water.			In methyl alcohol.		In ethyl alcohol.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 25^\circ$ (Ostwald)	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
32	50.00	91.83	91.8	45.97	63.51	14.29	21.99
64	51.49	94.62	94.5	50.12	69.32	15.60	24.85
128	52.51	98.00	97.7	53.95	74.51	17.52	27.72
256	53.40	99.68	100.0	56.67	80.57	19.39	30.84
512	54.70	101.3	101.5	60.06	83.31	21.36	33.25
1024	55.30	102.3	102.0	63.40	86.46	23.29	35.52

$\nu$	In ethyl alcohol (50 p. ct.) and water.		In methyl alcohol (25 p. ct.) and water.		In methyl alcohol (50 p. ct.) and water.		In methyl alcohol (75 p. ct.) and water.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
32	13.10	33.73	29.15	60.56	23.59	47.87	26.67	47.06
64	13.56	35.57	29.68	62.16	24.49	49.92	27.95	49.52
128	14.27	37.08	30.15	63.77	25.03	51.50	28.66	51.64
256	14.63	38.85	30.70	64.96	25.71	53.57	29.51	54.36
512	15.45	40.14	31.35	66.78	26.35	54.62	30.64	56.68
1024	16.25	41.35	32.56	69.02	27.35	55.60	31.91	58.56

TABLE 18. — *Temperature coefficients of conductivity of lithium nitrate.*

$\nu$	In water (0° to 25°).	In methyl alcohol (0° to 25°).	In ethyl alcohol (0° to 25°).	In ethyl alcohol (50 p. ct.) and water (0° to 25°).	In methyl alcohol (25, 50, and 75 p. ct.) and water (0° to 25°).		
					25 p. ct.	50 p. ct.	75 p. ct.
32	1.67	0.702	0.308	0.83	1.25	0.97	0.82
64	1.72	.768	.370	.88	1.30	1.01	.86
128	1.82	.822	.408	.91	1.35	1.06	.92
256	1.85	.956	.458	.97	1.37	1.11	.99
512	1.86	.930	.476	.99	1.42	1.13	1.04
1024	1.88	.922	.489	1.04	1.46	1.13	1.07

TABLE 19. — *Comparison of the molecular conductivity of lithium nitrate in methyl alcohol, water, and mixtures of these solvents.*

$\nu$	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	57 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
32	50.00	29.15	23.59	26.67	45.97	91.83	60.56	47.87	47.06	63.51
64	51.49	29.68	24.49	27.95	50.12	94.62	62.16	49.92	49.52	69.32
128	52.51	30.15	25.03	28.66	53.95	98.00	63.77	51.50	51.64	74.51
256	53.40	30.70	25.71	29.51	56.67	99.68	64.96	53.57	54.36	80.57
512	54.70	31.35	26.35	30.64	60.06	101.3	66.78	54.62	56.68	83.31
1024	55.30	32.56	27.35	31.91	63.40	102.3	69.02	55.60	58.56	86.46

These values, table 19, when plotted (figs. 7 and 8), give curves very similar to those already described in connection with potassium iodide and strontium iodide. The only difference worthy of special mention is the fact that at 0° the molecular conductivity in methyl alcohol rises above that in water.

## FERRIC CHLORIDE.

It was desired to make a complete investigation of the changes in the conductivity of solutions of ferric chloride in the various solvents. This was desirable on account of the great solubility of the substance in the different alcohols, and because of the large number of ions into which it can dissociate. This part of the investigation had to be postponed. Some few observations were, however, made, and these are recorded. The ferric chloride used was

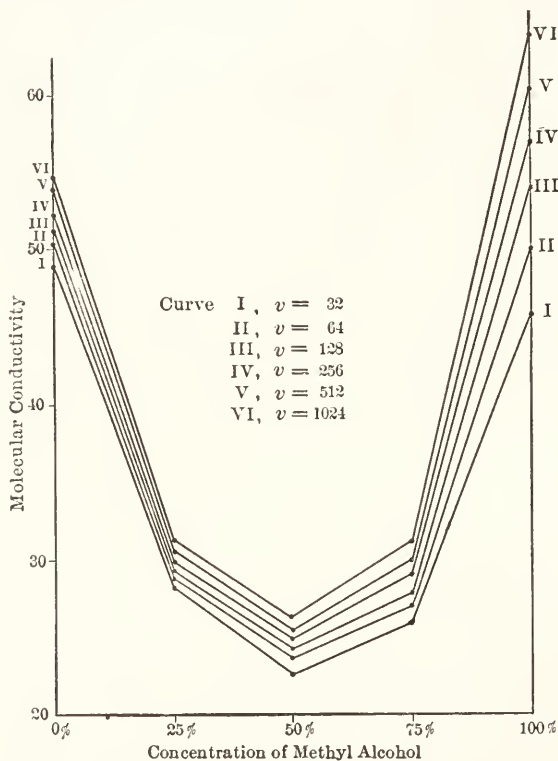


FIG. 7. — LITHIUM NITRATE AT 0°.

prepared as follows: Iron filings, which had been washed with alcohol and ether to remove any adhering grease, were heated in a current of pure, dry chlorine, in a large combustion tube of hard glass. The ferric chloride formed was allowed to distill into a cooled portion of the tube, and then it was redistilled into a wide-mouthed salt bottle. The excess of chlorine was removed by heating the chloride in a current of dry nitrogen. The chloride thus formed dissolved completely in both alcohol and water.

Water solutions were standardized as follows: They were reduced with zinc and sulphuric acid, and the ferrous iron determined with standard



potassium permanganate. Alcoholic solutions were first precipitated with aqueous ammonia; filtered, washed, dissolved in a little hydrochloric acid, reduced, and titrated as above.

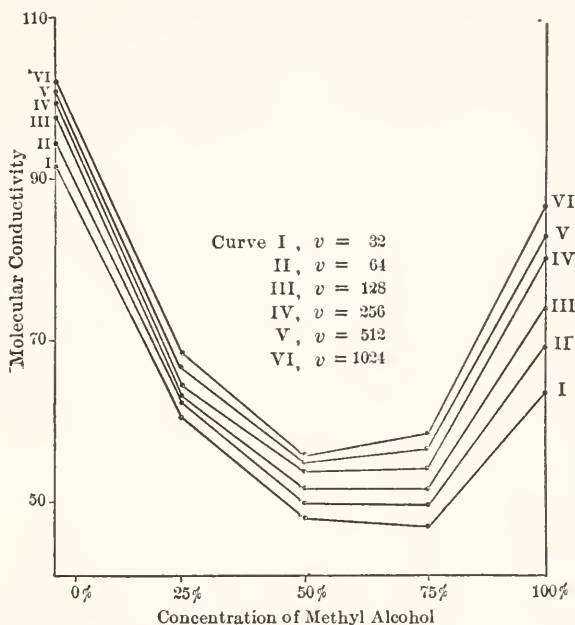


FIG. 8. — LITHIUM NITRATE AT 25°.

The values in table 20 agree fairly well with those found by Goodwin,<sup>1</sup> but are in all cases slightly lower, possibly due to the fact that the conductivity of our solutions was measured immediately after standardization, while those used by Goodwin had been made up for several months. Accurate measurements at a dilution greater than  $v = 256$  could not be made, since hydrolysis took place to a very marked extent, as was noticed by Goodwin in the work just referred to.

TABLE 20. — Conductivity of ferric chloride in water.

$v$	Molecular conductivity.		Temperature coefficient (0° to 25°).
	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	
32	163.7	319.2	6.22
64	187.0	370.2	7.32
128	213.0	422.6	8.38
256	240.0	476.7	9.47

<sup>1</sup> Phys. Rev., **11**, 193 (1900); Ztschr. phys. Chem., **21**, 1 (1896).

In mixtures of the alcohols and water the same hydrolysis was found to take place, while in the solutions in absolute alcohol a different change occurred. The solution, originally of a pale straw color, gradually became lighter and lighter when in contact with the platinum black of the electrodes. This was accompanied by a steady rise in the molecular conductivity, which, at the end of 24 hours, was still appreciable. The colorless solution showed only the slightest trace of ferric iron, having apparently been reduced to the ferrous condition. These changes are shown in table 21.

TABLE 21. — *Changes in the molecular conductivity of ferric chloride ( $v = 512$ ), with time.*

In mixture of methyl alcohol (50 p.ct.) and water.		In methyl alcohol.	
Date.	$\mu_{v25^\circ}$	Date.	$\mu_{v25^\circ}$
April 8. 12 <sup>h</sup> 25 <sup>m</sup> p.m.	....	April 15. 2 <sup>h</sup> 15 <sup>m</sup> p.m.	.....
12 27	130.1	2 18	62.90
12 29	135.6	2 21	65.47
12 31	141.8	2 24	67.18
12 33	145.4	2 28	68.16
12 36	150.8	2 35	69.64
12 38	153.9	2 45	71.91
12 41	156.3	3 00	75.00
12 45	159.5	3 15	78.06
12 56	162.4	3 30	81.75
1 00	166.7	3 46	84.11
1 10	169.1	4 15	88.59
1 30	172.9	4 45	92.93
2 00	175.0	6 15	103.6
3 00	180.6	April 16. 10 35 a.m.	132.6
4 00	182.2	11 15	133.7
5 00	183.0	2 35 p.m.	134.3

#### SUMMARY.

The preceding investigation leads to the conclusion that the minimum point, discovered by Zelinsky and Krapiwín, is not an isolated phenomenon restricted to the mixtures of methyl alcohol and water, but is much more general. This minimum point in the conductivity has been found for all the salts studied in mixtures of methyl alcohol and water, with the exception of cadmium iodide. Ethyl alcohol and water yield a minimum in the conductivity of all the salts investigated at 0°. At 25° this minimum had disappeared. Mixtures of methyl alcohol and ethyl alcohol do not exhibit this phenomenon, but the conductivity of a salt dissolved in a 50 per cent mixture of methyl and ethyl alcohols is less than the mean of the conductivities of the substance in the pure solvents at the same dilution.

To explain these facts we advance tentatively the following suggestion: According to the theory of Dutoit and Aston it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes. If this

be true, it is probable, since those substances which dissociate dissolved electrolytes also show in general a normal molecular weight for dissolved non-electrolytes, that this breaking down of the polymerized molecule can be accomplished best by another associated molecule. From this it follows that the effect of mixing two associated solvents would be to lower the state of association of one or both until a state of equilibrium is reached. Such a mixture would be that of water and either methyl or ethyl alcohol, or a mixture of methyl alcohol and ethyl alcohol. In these cases, since the molecules are less associated than the constituents, we should expect dissolved electrolytes to show a conductivity lower than that required by the law of mixtures. In every solvent with which we have worked this is exactly what has been observed. In the mixtures of methyl alcohol and water, where the association of the constituents is the greatest, the lowering of conductivity is also the greatest, as would be expected.

In support of the above view that one associated solvent can diminish the association of another associated solvent, we have experimental evidence in the results of freezing-point measurements. The molecular weights of the alcohols in water, as determined by the freezing-point method, are normal; while the surface-tension method of Ramsay and Shields shows, beyond question, that the alcohols are associated compounds.

The effect of temperature on the lowering of the conductivity is in accord with the above suggestion. Since the effect of rise in temperature is to lower the state of aggregation of an associated liquid, it would be expected that at the higher temperature the influence of the solvents on each other would be less than at the lower temperature. That such is the case can be seen by comparing the results at 0° with those at 25°.

The conclusion reached from this investigation, that one associated solvent can diminish the association of another associated solvent, was subsequently confirmed by the work of Jones and Murray.<sup>1</sup> They worked with water, and formic and acetic acids, and determined the molecular weight of each in the other by the freezing-point method. These, as is well known, are all strongly associated substances when in the pure, homogeneous condition.

Jones and Murray found that the molecular weights of these substances, in the most concentrated solutions which could be studied, were always less than the molecular weights of the pure substances as determined by the method of Ramsay and Shields;<sup>2</sup> and, further, the molecular weights decreased in every case with increase in the dilution of the solution, as would be expected from the law of mass action. Both of these facts point to the same conclusion, viz, that one associated solvent breaks down the complex molecules of another associated solvent into simpler molecules.

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<sup>1</sup> Amer. Chem. Journ., **30**, 193 (1903).

<sup>2</sup> Ztschr. phys. Chem., **12**, 433 (1893).

The action of one associated solvent on another associated solvent will be seen to be analogous to the action of an associated solvent on an electrolyte, if we take into account that an associated solvent is a non-electrolyte.

An associated solvent breaks the molecules of an electrolyte down into ions. An associated solvent breaks the complex molecules of a non-electrolyte down into simpler molecules, which is the nearest approach to ions that can be obtained from a non-electrolyte.

## WORK OF CARROLL.

The first part of this work is a continuation of the investigation of Jones and Lindsay.

### EXPERIMENTAL.

#### APPARATUS.

The Kohlrausch method of measuring conductivity was used throughout this investigation. The bridge-wire was of "manganin." The resistance coils were carefully calibrated. The conductivity cells were of the form used by Jones and Lindsay. The constants of these were determined by means of N/50 and N/500 solutions of potassium chloride. Cells used to determine conductivities of the solvent and of highly diluted solutions were treated in the manner recommended by Whetham.<sup>2</sup> The electrodes were first coated with platinum black in the usual manner, and were afterwards heated to a high temperature in the flame of a blast-lamp. It was found, as Whetham states, that the usual coating of platinum black, in spite of careful and long-continued washing, retains traces of salt that subsequently pass slowly into solution. The oxidizing action of the platinum black is also avoided by this treatment. For the purposes mentioned, electrodes of this kind can not be too highly recommended. The tone-minimum in the telephone is fully as good as with the ordinary type of electrode.

The 25° thermostat was of the usual (Ostwald) form, and the stirrer was driven by a small hot-air motor. The zero-bath was of the type used by Jones and Lindsay, consisting of an outer and an inner vessel. The inner vessel and the annular space between the two were filled with finely crushed ice. The outer portion of ice was moistened with a small quantity of distilled water, and to the ice in the inner vessel about an equal weight of water was added. By the foregoing means the temperature of a cell immersed in the ice and water of the inner vessel could be kept for any desired period at 0.02° to 0.05° C.

The measuring flasks, pipettes, and burettes were carefully calibrated.

#### SOLVENTS.

The water used was purified in the following manner: Ordinary distilled water, after addition of potassium dichromate and sulphuric acid, was re-distilled. The distillate was again distilled from chromic acid into, and then out of, a solution of barium hydroxide. When the conductivity of the water thus obtained was greater than  $2 \times 10^{-6}$ , the above process was repeated. In many cases the conductivity was much less than this value.

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<sup>1</sup> Amer. Chem. Journ., **28**, 329 (1902).

<sup>2</sup> Phil. Trans., **94** (A), 321 (1900). Ztschr. phys. Chem., **33**, 346 (1900).

The methyl and ethyl alcohols were prepared from the purest commercial preparations obtainable. Each was subjected to the same treatment. The commercial alcohol was dehydrated by standing in contact with freshly burned lime for several weeks. From this it was distilled, and then allowed to stand over dehydrated copper sulphate for a week or more. When required for use, it was distilled from the copper sulphate, small quantities of sodium being added, and precautions were taken to protect the distillate from access of moisture.

The conductivity of the methyl alcohol thus obtained was usually from 1 to  $2 \times 10^{-6}$ . That of the ethyl alcohol was less.

The acetic acid used was obtained from Bender and Hobein, and was designed for cryoscopic work. The amount of water contained in it was determined, as suggested by Rudorf, by observation of its freezing-point. Its conductivity was less than  $2 \times 10^{-6}$ .

#### METHOD OF PREPARING THE SOLUTIONS.

The mixtures of solvents were prepared as follows:  $n$  c. c. of alcohol, for example, were diluted to, say, 100 c. c. This is designated as a mixture of  $n$  per cent alcohol. Calibrated flasks were used for the dilutions, and the temperature was kept within a few tenths of a degree of the temperature of calibration. In making up the solutions, the exact amount of the salt in question was put into a measuring-flask, and after adding a portion of the solvent, the substance was dissolved and the flask filled to the mark. Here also the temperature was kept under control.

Usually, the original solutions were N/16 or N/32. From these, others were made by adding the solvent to a measured portion of the solution. Where the quantity to be used would be too small to be measured with reasonable accuracy, one of the intermediate solutions was taken as a starting-point for further dilution.

#### CONDUCTIVITY MEASUREMENTS

The constants of the cells used were determined or checked at intervals of a few days. For each conductivity determination, from three to seven or eight different resistances were used. The values given in the tables are, therefore, the mean of several determinations. Conductivities throughout are expressed as molecular conductivities.

#### CADMIUM IODIDE.

The cadmium iodide used was a preparation of which a part had been used by Jones and Lindsay in their work.

Jones and Lindsay measured the conductivity of cadmium iodide in water, methyl alcohol, and mixtures at 25° only. The minimum was not observed. It seemed desirable, therefore, to complete the study of the compound.

The cadmium iodide was dried by being allowed to stand in a desiccator over calcium chloride for a week or more. At first the attempt was made to

dry it by prolonged heating in an air-bath at 70° to 80°. It was found that when thus treated, the salt assumed a pinkish hue, which immediately gave place to the pinkish white of the salt in the ordinary condition when a small quantity of water was added. No mention of this color change can be found in the literature. Though no traces of decomposition could be detected, the other method of drying was chosen. The original solutions were made by direct weighing.

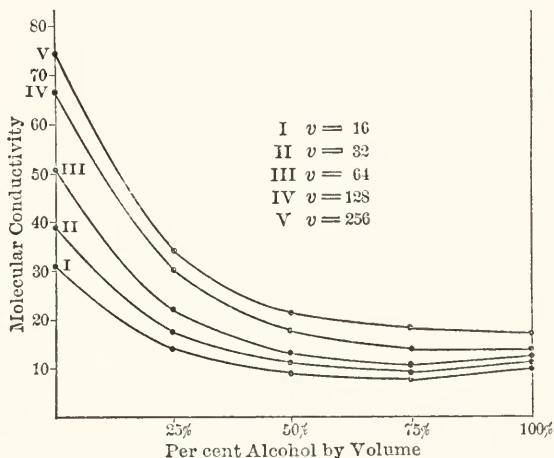


FIG. 9. — CONDUCTIVITY OF CADMIUM IODIDE IN WATER, METHYL ALCOHOL, AND MIXTURES AT 0°.

TABLE 22. — Conductivity of cadmium iodide.

$v$	In water at 0° and 25°.			In 25 p. ct. methyl alcohol at 0° and 25°.			In 50 p. ct. methyl alcohol at 0° and 25°.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
16	31.16	62.86	1.268	14.57	33.83	0.770	9.96	20.82	0.434
32	40.07	81.82	1.670	17.68	42.10	0.977	11.23	24.21	0.519
64	51.93	107.77	2.114	22.68	55.02	1.294	14.21	31.25	0.682
128	63.85	130.24	2.666	28.59	70.22	1.665	18.92	41.61	0.908
256	76.54	155.55	3.160	35.36	87.31	2.078	21.58	51.4	1.193

$v$	In 75 p. ct. methyl alcohol at 0° and 25°.			In 100 p. ct. methyl alcohol at 0° and 25°.			In ethyl alcohol, $\mu_v 25^\circ$ .			
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
16	8.94	15.78	0.274	10.96	13.39	0.097	26.97	14.03	9.43	2.29
32	9.71	17.08	.295	11.55	14.51	.118	34.90	16.19	9.52	2.30
64	11.24	20.08	.354	12.66	14.83	.087	44.21	18.93	10.94	2.32
128	14.37	25.68	.452	13.69	16.82	.124	54.54	25.66	12.27	2.39
256	18.58	33.52	.598	17.62	20.01	.096	69.71	34.89	15.16	2.66

From the data given, especially in table 23, it is seen that cadmium iodide does not show the minimum in mixtures of methyl alcohol and water at 25°. At 0°, however, in a 75 per cent mixture, at volumes 16, 32, and 64, the minimum appears. Beyond these concentrations it disappears.

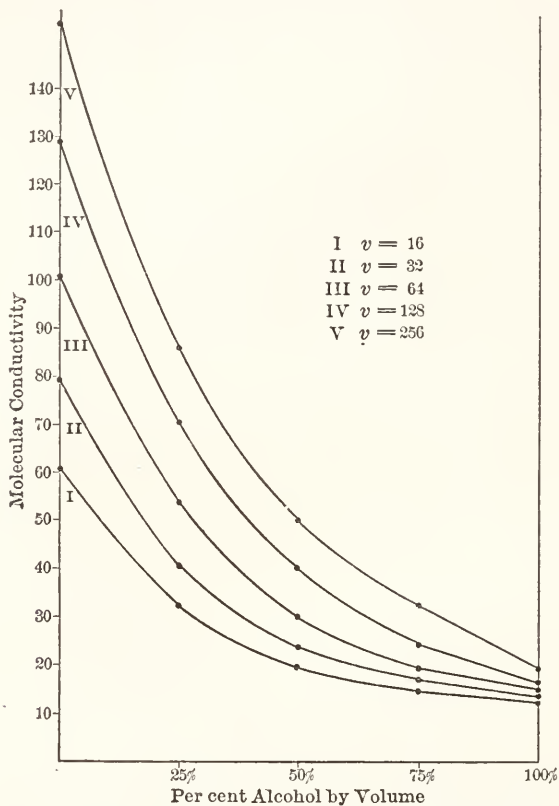


FIG. 10.—CONDUCTIVITY OF CADMIUM IODIDE IN WATER, METHYL ALCOHOL, AND MIXTURES AT 25°.

In various mixtures of ethyl alcohol and water at 25° (table 23) no minimum appears, although the values observed are in all cases less than would be expected from the rule of averages. The results are plotted as curves in figs. 9 and 10, the ordinates being conductivities and the abscissæ representing the per cent by volume of alcohol.



TABLE 23. — Comparison of conductivities.

<i>v</i>	Cadmium iodide in methyl alcohol.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH
16	31.16	14.57	9.96	8.94	10.96	62.86	33.83	20.82	15.78	13.39
32	40.07	17.68	11.23	9.71	11.55	81.82	42.10	24.21	17.08	14.51
64	51.93	22.68	14.21	11.28	12.66	104.77	55.02	31.25	20.08	14.83
128	68.53	31.09	18.92	14.37	13.69	130.24	70.22	41.61	25.68	16.82
256	76.54	35.36	21.58	18.58	17.62	155.55	87.31	51.40	33.52	20.01

<i>v</i>	Cadmium iodide in ethyl alcohol at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. C <sub>2</sub> H <sub>5</sub> OH
16	62.86	26.97	14.03	9.43	2.29
32	81.82	34.90	16.19	9.52	2.30
64	104.77	44.21	18.93	10.94	2.32
128	130.24	54.54	25.66	12.27	2.39
256	155.55	69.71	34.89	15.16	2.66

## SODIUM IODIDE.

The sodium iodide used was a preparation that had been carefully purified by Jones and Lindsay. The salt was dried in an air-bath for three days at a temperature of 110° to 130°. This prolonged treatment was found necessary to bring it to constant weight. The original solutions were made up by direct weighing.

TABLE 24. — Conductivity of sodium iodide at 0° and 25°.

<i>v</i>	In water.				In 25 p. ct. methyl alcohol.		
	$\mu_0$	$\mu_{25}$	$\mu_{25}(0)$	Temperature coefficient. <sup>1</sup>	$\mu_0$	$\mu_{25}$	Temperature coefficient.
32	57.46	106.0	105.7	1.942	33.63	70.62	1.48
64	59.37	109.35	109.3	2.000	34.68	72.77	1.52
128	60.71	112.44	112.3	2.069	35.63	73.78	1.53
256	62.35	115.5	115.2	2.126	36.73	74.32	1.504
512	64.28	118.08	117.9	2.152	37.83	74.98	1.49

<i>v</i>	In 50 p. ct. methyl alcohol.			In 75 p. ct. methyl alcohol.			In 100 p. ct. methyl alcohol.		
	$\mu_0$	$\mu_{25}$	Temperature coefficient.	$\mu_0$	$\mu_{25}$	Temperature coefficient.	$\mu_0$	$\mu_{25}$	Temperature coefficient.
32	27.91	57.18	1.171	31.70	56.50	0.992	51.09	72.03	0.838
64	28.73	58.30	1.183	33.08	59.47	1.056	55.95	77.63	0.867
128	29.04	59.16	1.205	34.16	61.49	1.093	58.89	82.70	0.955
256	30.32	60.87	1.232	34.72	62.74	1.121	61.02	86.19	1.009
512	32.08	61.62	1.181	35.00	63.77	1.151	62.56	88.27	1.026

<sup>1</sup> These values are those given by Ostwald [Ztschr. phys. Chem., 7, 74 (1887)]. The agreement is seen to be quite satisfactory.

<sup>2</sup> The values at 0° are uncorrected for conductivity of solvent.

TABLE 25. — Comparison of conductivities.

$v$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH	
At 0°	32	57.46	33.63	27.91	31.70	51.09
	64	59.37	34.68	28.73	33.08	55.95
	128	60.71	35.63	29.04	34.16	58.89
	256	62.35	36.73	30.32	34.72	61.02
	512	64.28	37.83	32.08	35.00	62.56
At 25°	32	106.0	70.62	57.18	56.50	72.03
	64	109.35	72.77	58.30	59.47	77.63
	128	112.44	73.78	59.16	61.49	82.76
	256	115.49	74.33	60.87	62.74	86.19
	512	118.08	74.98	61.62	63.77	88.27

From the data given in table 25, and from the curves plotted in the manner already indicated (fig. 11), it is evident that sodium iodide exhibits the

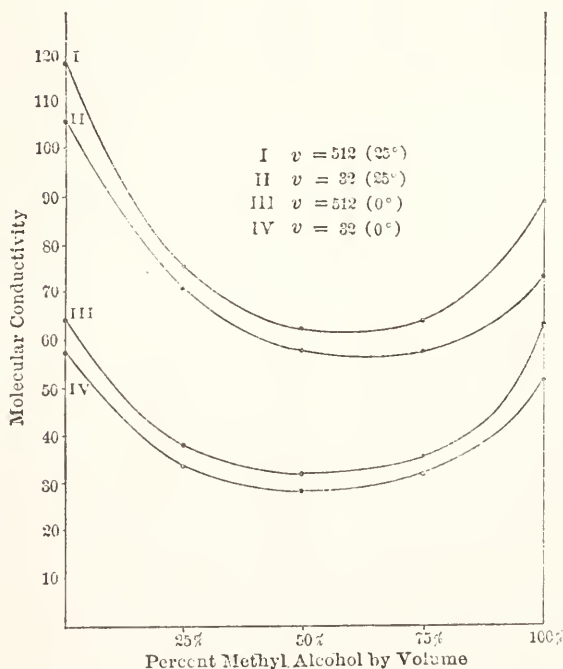


FIG. 11. — CONDUCTIVITY OF SODIUM IODIDE IN MIXTURES OF METHYL ALCOHOL AND WATER.

minimum in mixtures of methyl alcohol and water. Only two dilutions at the two temperatures of observation have been plotted, since the curves would be too close together if all were shown.

The minimum, as Jones and Lindsay have observed in other cases, is more pronounced at 0° than at 25°. Further, the shifting effect of change of temperature and of concentration, also observed by Jones and Lindsay, appears at 25°,  $v = 32$ . The minimum occurs in a 75 per cent mixture; beyond this dilution the minima occur solely in the 50 per cent mixture. At 0° the minimum appears to be exhibited in the 50 per cent mixture alone.

## CALCIUM NITRATE.

It was thought that the study of a ternary salt might prove interesting. Jones and Lindsay had already made a study of strontium iodide, and had found it to exhibit the same phenomena as did binary salts.

The calcium nitrate used was a preparation obtained from Kahlbaum. This substance was found to be particularly difficult to dehydrate. Heating for several days to a temperature of 103° to 140° was necessary to bring it to constant weight. This treatment caused no perceptible decomposition. All the original solutions were made by direct weighing.

TABLE 26. — *Conductivity of calcium nitrate.*

$\nu$	In water at 0° and 25°.			In 25 p. ct. methyl alcohol at 0° and 25°.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
16	94.33	177.56	3.329	53.17	111.45	2.333
32	102.47	189.45	3.440	57.30	120.63	2.533
64	108.35	199.24	3.636	59.81	128.95	2.776
128	113.59	209.93	3.854	63.39	136.81	2.937
256	118.02	215.93	3.916	66.19	141.45	3.010

$\nu$	In 50 p. ct. methyl alcohol at 0° and 25°.			In 75 p. ct. methyl alcohol at 0° and 25°.			In 100 p. ct. methyl alcohol at 0° and 25°.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temp. coef.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temp. coef.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temp. coef.
16	41.07	79.04	1.518	39.59	70.06	1.219	....	32.79	....
32	44.70	90.11	1.816	43.60	80.16	1.462	31.30	41.88	0.423
64	49.15	98.35	1.968	48.58	89.98	1.645	37.27	50.79	.541
128	53.94	103.68	1.990	51.90	97.72	1.883	46.66	60.52	.555
256	54.82	109.19	2.175	....	....	....	55.17	73.98	.752

$\nu$	In 25 p. ct. ethyl alcohol at 0° and 25°.			In 50 p. ct. ethyl alcohol at 0° and 25°.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
16	38.80	92.93	2.065	23.70	60.43	1.469
32	41.84	100.56	2.359	25.89	65.30	1.576
64	....	....	....	27.37	69.83	1.698
128	48.02	112.93	2.596	28.83	74.13	1.812
256	50.26	119.04	2.750	30.30	78.31	1.920

$\nu$	In 75 p. ct. ethyl alcohol at 0° and 25°.			In 100 p. ct. ethyl alcohol at 0° and 25°.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
16	19.13	39.08	0.798	4.89	7.08	0.088
32	21.41	44.57	0.926	7.11	9.57	.098
64	....	....	....	8.59	12.43	.153
128	26.71	56.08	1.175	10.74	15.47	.189
256	28.61	60.79	1.287	12.48	18.57	.244

TABLE 27. — Comparison of conductivities.

Calcium nitrate in methyl alcohol.										
<i>v</i>	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH
16	94.33	53.17	41.07	39.59	....	177.56	111.45	79.04	70.06	32.79
32	102.47	57.30	44.70	43.60	31.30	189.45	120.63	90.11	80.16	41.88
64	108.35	59.81	49.15	48.85	37.27	199.24	128.95	98.35	89.98	50.79
128	113.59	63.39	53.94	51.90	46.66	209.93	136.81	103.68	97.72	60.52
256	118.02	66.19	54.82	....	55.17	215.93	141.45	109.19	....	73.98

Calcium nitrate in ethyl alcohol.										
<i>v</i>	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. C <sub>2</sub> H <sub>5</sub> OH	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. C <sub>2</sub> H <sub>5</sub> OH
16	94.33	38.80	23.70	19.13	4.89	177.56	92.93	60.43	39.08	7.08
32	102.47	41.84	25.89	21.41	7.11	189.45	100.56	65.30	44.57	9.57
64	108.35	....	27.37	....	8.57	199.24	....	69.83	....	12.43
128	113.59	48.02	28.83	26.71	10.74	207.93	112.93	74.13	56.08	15.47
256	118.02	50.26	30.30	28.61	12.48	215.93	119.04	78.31	60.79	18.57

From the data given in table 27, it is evident that calcium nitrate in no case exhibits the minimum. The conductivities are always less than the proper average.

The relation found by Wakeman,  $\frac{\Delta}{p(100-p)} = \text{const.}$  does not hold in the cases thus far studied; nor does that found by Cohen.

#### HYDROCHLORIC ACID.

In the study of hydrochloric acid the solutions were prepared as follows: Into a portion of the solvent, kept cool by ice, dry hydrochloric-acid gas was conducted. This was obtained by allowing concentrated sulphuric acid to drop slowly from a dropping-funnel into pure, aqueous, hydrochloric acid. The gas was dried by passing through gas-washing bottles containing concentrated sulphuric acid. The vessel containing the solvent into which the gas was passed, was protected from extraneous moisture by a drying-tube containing phosphorus pentoxide.

The strength of the original solution was determined volumetrically by means of a standard solution of ammonium hydroxide, methyl orange being used as the indicator. From this solution the dilutions were made. Control determinations were carried out in a number of cases, since only the fairly dilute solutions in mixtures and in pure methyl alcohol were found to be stable.

The composition of the 69.75 per cent mixture was determined by means of its specific gravity.

TABLE 28. — Conductivity of hydrochloric acid.

In 50 p. ct. methyl alcohol at 25°.		In 69.75 p. ct. methyl alcohol at 0° and at 25°.		
$v$	$\mu_{v25^\circ}$	$v$	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$
33.05	172.45	44.67	63.83	116.0
132.21	166.09	92.42	67.06	123.77
264.42	165.30	178.75	66.49	117.8
528.83	155.29	357.5	64.66	118.1
		714.72	66.19	116.87

In 90 p. ct. methyl alcohol at 0° and 25°.			In 100 p. ct. methyl alcohol at 0° and 25°.		
$v$	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	$v$	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$
31.53	46.59	73.79	8.42	67.36	95.83
63.07	47.60	76.19	32.8	77.06	110.50
157.67	51.84	84.27	130.26	79.84	118.79
252.28	51.84	84.27	481.44	89.79	129.87
504.56	....	84.22	2104.0	95.46	133.44

A consideration of the results, table 28, shows that in certain cases they are irregular and unexpected. In the 50 per cent mixture the conductivity falls from the first dilution, which is analogous to what has been observed for hydrochloric acid in ether and isoamyl alcohol by Cattaneo and Kablukoff, and for sulphuric acid in acetic acid by Jones—the molecular conductivities decreased for decreasing dilution. In the 69.75 per cent mixture a maximum is reached at  $v = 92.42$  at both 0° and 25°. From this point the conductivities decrease slightly. However, at 0° the mean of the last four conductivities, including the maximum, differs from the maximum value by only 1.5 per cent.

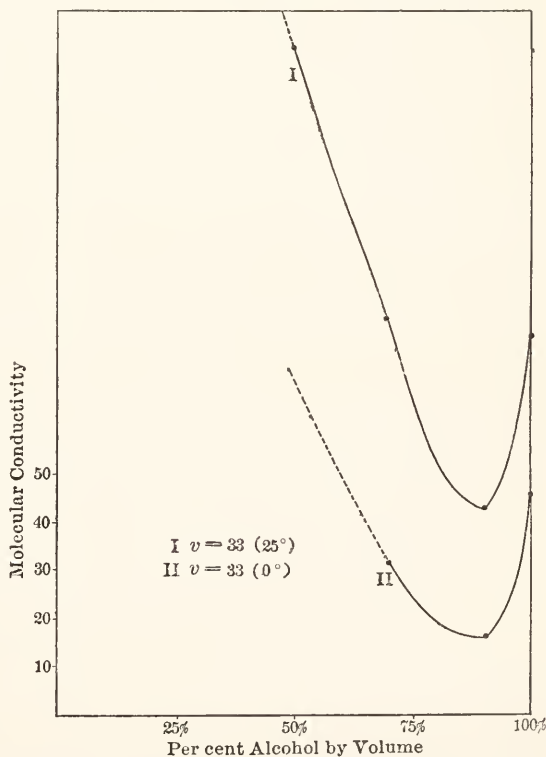


FIG. 12. — CONDUCTIVITY OF HYDROCHLORIC ACID IN MIXTURES OF METHYL ALCOHOL AND WATER.

In the 90 per cent mixture the results are perfectly regular, and, what is surprising, a limiting value is reached at  $v = 157.67$ .

In methyl alcohol the results are also regular, but there is no indication of a maximum value for conductivity. The values found agree in most cases very well with those of Carrara, whose results are also irregular (see fig. 12).

#### SODIUM ACETATE IN MIXTURES OF ACETIC ACID AND WATER.

The acetic acid froze at  $15.47^\circ$ . From the tables of Rüdorff it contained in 100 parts by weight, 0.6 part by weight of water. Knowing the composition of the acid, the proper amounts to be used in making the mixtures could be calculated.

The acid was partially frozen and the liquid portion rejected. After melting the solid acid the process was repeated. The specimen thus obtained was used for the conductivities in the pure solvent. Owing to inevitable exposure to the moisture of the air, it was not thought profitable to try to remove the last traces of moisture.

In this part of the problem new complications arose, since acetic acid in aqueous solution conducts the current.

The specific conductivity of the solvent (containing 25, 50, 75, and 100 per cent by volume of acetic acid) was determined; then that of the solution in question. The difference between the latter and the former was multiplied by the volume to give the (apparent) molecular conductivity.

The sodium acetate used was a specimen of the fused salt obtained from Kahlbaum. It was dried for two days in an air-bath at  $120^\circ$  to  $130^\circ$ . The original solutions were made up by direct weighing.

TABLE 29. — *Conductivity of sodium acetate.*

	$v$	Specific conductivity of solution.	$\mu_r, 25^\circ$ .
In 25 p. ct. acetic acid at $25^\circ$ (specific conductivity of solvent = 1.631) . .	{ 32	2.040	17.89
	{ 64	1.469	-10.37
In 50 p. ct. acetic acid at $25^\circ$ (specific conductivity of solvent = 0.8584). .	{ 32	1.388	16.84
	{ 64	0.9263	4.36
	{ 128	0.8986	5.15
In 75 p. ct. acetic acid at $25^\circ$ (specific conductivity of solvent = 0.0558). .	{ 32	0.7050	20.77
	{ 64	0.4446	24.87
	{ 128	0.2999	31.24
In acetic acid at $25^\circ$ (conductivity of solvent = $1 \times 10^{-6}$ ) . . . . .	{ 32	0.00418	0.134
	{ 64	0.00236	0.161
	{ 128	0.00129	0.165

The results are seen to be irregular, and no final conclusions can be drawn from them. In the 25 per cent mixture for  $v = 64$ , the molecular conductivity is apparently negative. This, of course, means nothing more than that the specific conductivity of the solvent is greater than that of the solution.

Only in the 75 per cent mixture is there any regularity observed. Here the (apparent) molecular conductivities increase with decreasing concentration.

In the pure solvent the conductivities are so small as to be almost negligible. This is not surprising. Wakeman<sup>1</sup> has determined the conductivity of hydrochloric acid in acetic acid, and has found it to be exceedingly small. For example, for  $v = 98.56 \mu_v$  was found to be 1.78.

The irregular results in mixtures of acetic acid and water are to be explained as being due to mutual isohydric influence of dissolved substance and solvent. The dissociation of the sodium acetate is driven back by the acetic acid, and *vice versa*. This influence is most marked where the dissociation of each separately would be greatest, *i. e.*, in mixtures of lower per cent of acetic acid, and of minimal concentration of sodium acetate.

Since these phenomena have no direct connection with the problem in hand, no further discussion is necessary, especially as the question has been treated by Wolf<sup>1</sup> and by Rüdorff.<sup>2</sup>

#### DISSOCIATION IN FIFTY PER CENT METHYL ALCOHOL.

It has been seen that in the case of hydrochloric acid in mixtures of methyl alcohol and water, limiting values for conductivity are reached at a smaller dilution than in either water or methyl alcohol. It is important to see whether this relation is general.

The limiting values in the case of sodium and potassium iodides and potassium bromide were determined. Throughout this part of the work the utmost care was taken in the preparation of solvents and solutions, and in making the dilutions. The cells used were standardized before and after each series of measurements. The conductivity of the solvent was carefully determined, and the necessary corrections were made. The water and the methyl alcohol used had a conductivity of not over  $1 \times 10^{-6}$ . Every result given is the mean of from five to ten different values.

#### POTASSIUM IODIDE.

The potassium iodide was prepared by Kahlbaum. The flame test showed that no appreciable impurity was present. The salt was dried to constant weight at 100° to 110°. The values obtained are given:

$v$	$\mu_v 25^\circ$
400	69.29
2000	70.58
4000	70.60

The value for the conductivity at  $v = 400$  agrees with the (interpolated) value obtained by Zelinsky and Krapiwın, and our results may therefore be

<sup>1</sup> Ztschr. phys. Chem., **15**, 181 (1894).

<sup>2</sup> Loc. cit.

incorporated with theirs. This has been done in table 30. The degree of dissociation has been calculated for each dilution. Included in the table, for comparison, are similar values calculated from data obtained by Ostwald for potassium iodide in water, and from data given by Carrara for potassium iodide in methyl alcohol.

TABLE 30. — *Conductivity and dissociation of potassium iodide in water, methyl alcohol, and 50 per cent methyl alcohol.*

$v$	Conductivity of potassium iodide in water, methyl alcohol, and 50 p. ct. methyl alcohol, at 25°.			Dissociation of potassium iodide in water, methyl alcohol, and 50 p. ct. methyl alcohol.		
	H <sub>2</sub> O $\mu_v 25^\circ$	50 p. ct. CH <sub>3</sub> OH $\mu_v 25^\circ$	CH <sub>3</sub> OH $\mu_v 25^\circ$	H <sub>2</sub> O $\alpha$	50 p. ct. CH <sub>3</sub> OH $\alpha$	CH <sub>3</sub> OH $\alpha$
16	124.5	62.13	68.14	0.873	0.880	0.697
32	128.5	64.37	74.42	.900	0.912	.762
64	130.5	66.01	79.85	.915	0.936	.818
128	133.0	67.45	84.70	.931	0.956	.868
256	135.8	68.28	88.25	.953	0.968	.904
400	....	69.20	....	....	....	....
512	137.9	69.65	90.82	.967	0.987	.931
1024	140.9	70.55	93.07	.989	1.000	.954
2000	....	70.58	....	....	....	....
4000	....	70.60	....	....	....	....
$\infty$	142.6	70.58	97.63	....	....	....

The values of the dissociation factors are shown in table 30. From an inspection of the data, it is seen that a limiting value for conductivity is reached at a lower dilution in the mixture than in the other solvents.

An inspection of this table shows that, at corresponding dilutions, *dissociation as calculated from conductivity is greater in the mixture than in methyl alcohol or in water.* The only other solvent thus far shown to have a greater dissociating power than water is liquid hydrocyanic acid, as appears from the work of Centnerszwer. Potassium iodide was one of the substances used.

#### SODIUM IODIDE.

The sodium iodide was the preparation previously employed. The accompanying measurements were made:

$v$	$\mu_v 25^\circ$
500	60.92
2000	61.72
4000	61.65

Combining these with the values previously obtained, and using Carrara's values for conductivities in water and methyl alcohol, respectively, we have the values given in table 31.



TABLE 31. — *Conductivity and dissociation of sodium iodide in water, methyl alcohol, and 50 per cent methyl alcohol.*

$v$	Conductivity of sodium iodide in water, methyl alcohol, and 50 p. ct. methyl alcohol, at 25°. <sup>1</sup>			Dissociation of sodium iodide in water, methyl alcohol, and 50 p. ct. methyl alcohol. <sup>2</sup>		
	H <sub>2</sub> O $\mu_v 25^\circ$	50 p. ct. CH <sub>3</sub> OH $\mu_v 25^\circ$	CH <sub>2</sub> OH $\mu_v 25^\circ$	H <sub>2</sub> O $\alpha$	50 p. ct. CH <sub>3</sub> OH $\alpha$	CH <sub>2</sub> OH $\alpha$
32	106.0	57.18	68.75	0.865	0.927	0.766
64	109.3	58.30	73.11	.901	.946	.816
128	112.4	59.16	77.31	.917	.959	.861
256	115.5	60.87	79.90	.949	.987	.890
512	118.1	61.27	82.15	.971	.993	.915
2000	....	61.72	....	....	1.000	....
4000	....	61.65	....	1.000	1.000	....
$\infty$	121.4	61.68	89.77	....	....	....

<sup>1</sup> It is evident, in this case, that the results are of the same general character as those found for potassium iodide.

<sup>2</sup> Here also, as was found for potassium iodide, the dissociation is greater in the mixture.

The accompanying measurements were made for potassium bromide in 50 per cent methyl alcohol:

$v$	$\mu_v 25^\circ$
250	65.78
1250	69.26
2500	69.35

At  $v = 250$  the dissociation is 0.949 for the mixture.

At  $v = 256$  the dissociation is 0.927 for water, and 0.806 for methyl alcohol, as calculated from Ostwald's <sup>1</sup> and Carrara's <sup>1</sup> observations.

The values for the dissociation constants are seen to be about the same as those for potassium iodide. Data for conductivity in aqueous solution could not be found. The values for methyl alcohol are calculated from Carrara's data; those for the mixture, from the results of Zelinsky and Krapivin.

TABLE 32. — *Dissociation of ammonium bromide, ammonium iodide, and lithium nitrate in 50 per cent methyl alcohol.*

$v$	Dissociation of ammonium bromide in 50 p. ct. methyl alcohol.	Dissociation of ammonium iodide in 50 p. ct. methyl alcohol.	Dissociation of lithium nitrate in 50 p. ct. methyl alcohol at 0° and at 25°.	
	50 p. ct. CH <sub>3</sub> OH $\alpha$	50 p. ct. CH <sub>3</sub> OH $\alpha$	$\alpha 0^\circ$	$\alpha 25^\circ$
16	0.871	0.875	....	....
32	0.910	0.909	0.863	0.862
64	0.942	0.943	0.899	0.899
128	0.962	0.967	0.915	0.926
256	0.974	0.973	0.944	0.964
512	0.986	0.994	0.963	0.982
1024	1.000	1.000	1.000	1.000

<sup>1</sup> Loc. cit.

In table 32 the values are about the same as for ammonium bromide. The data for the mixture and for methyl alcohol were furnished by Zelinsky and Krapivin and by Carrara, respectively.

From results given by Jones and Lindsay it is possible to calculate the dissociation of lithium nitrate in the 50 per cent mixture at two temperatures, 0° and 25°, assuming that here, as in the other cases, complete dissociation is reached at  $v = 1024$ . It is known that in aqueous solution complete dissociation is not reached as soon in the case of lithium salts as with potassium or sodium salts. Less value must therefore be attached to the results given in table 32.

Values of the dissociation for hydrochloric acid in the 90 per cent and in the 69.75 per cent mixtures at 0° and at 25° are also given in table 33. It will be remembered that the results in the latter mixture were irregular. No stress can, therefore, be laid upon these figures. We have taken the determinations for  $v = 92.4$  as the limiting values in this case.

TABLE 33. — *Dissociation of hydrochloric acid in 69.75 per cent and 90 per cent methyl alcohol, in water, and in methyl alcohol.*

$v$	69.75 p. ct. CH <sub>3</sub> OH		90 p. ct. CH <sub>3</sub> OH		H <sub>2</sub> O	CH <sub>3</sub> OH	
	$\alpha_0^\circ$	$\alpha_{25^\circ}$	$\alpha_0^\circ$	$\alpha_{25^\circ}$	$\alpha_{25^\circ}$	$\alpha_{25^\circ}$	$v$
31.5	....	....	0.900	0.875	0.909	0.890	37.74
44.67	0.981	0.937	....	....	....	0.916	75.47
63.0	....	....	0.919	0.924	....	....	....
92.42	1.000	1.000	....	....	....	0.972	150.9
158	....	....	1.000	1.000	....	....	....
252	....	....	1.000	1.000	0.934	....	....

The values for conductivities in water are taken from Ostwald;<sup>1</sup> those for methyl alcohol from Carrara.

It is observed in table 33 that the dissociation is greater in the 69.75 per cent mixture than in water at the corresponding dilution. This, however, is not the case for the 90 per cent mixture. It is also interesting to note that the dissociation is apparently greater at 0° than it is at 25°, and this is true for the 90 per cent mixture, where the results are more reliable than those for the 69.75 per cent mixture.

We have suggested that the dissociation in the 50 per cent mixture may be due in part to the presence of the hydrate CH<sub>3</sub>OH · 3H<sub>2</sub>O. This compound would be more stable at a lower than at a higher temperature, and would be present to a greater extent at the lower temperature, and therefore the dissociation might be greater. This result should be shown by salts as well as

<sup>1</sup> Journ. prakt. Chem., 140, 300 (1885).

by hydrochloric acid, but data are not at hand for comparison. Jones and Lindsay's values for lithium nitrate are available and have been used (table 29). From this table, apparently, the dissociation is greater at the higher temperature. But, as we have said, no final conclusions can be drawn from these data, since we can not be certain that limiting conductivity values were reached by Jones and Lindsay. In the case of hydrochloric acid, however, they were reached in at least one instance. Further investigation will be needed to decide this matter.

It is interesting at this point to see whether the hypothesis of Dutoit and Aston <sup>1</sup> is quantitatively true for the cases that have been considered. This hypothesis states that the dissociating power of a solvent is dependent upon its association, as determined by the surface-tension method of Ramsay and Shields.<sup>2</sup> If the hypothesis holds quantitatively, it may be formulated thus:  $\frac{a}{a'} = \frac{x}{x'}$ , where  $a$  and  $a'$  are the dissociations of the solutions compared, and  $x$  and  $x'$  the association factors of the solvents. The relation may be put into the form  $\frac{a}{x} = \text{constant}$ .

In comparing solutions in different solvents, there should be the same number of gram-molecules of electrolyte dissolved in the same number of gram-molecules of each solvent. Where solutions in water, methyl alcohol, and ethyl alcohol are to be compared, the volumes will have the ratio 18, 40, and 58 approximately.

A comparison is made on this basis for potassium and sodium iodides in water and methyl and ethyl alcohols (table 34). For the ethyl alcohol solution the dissociation was calculated from the data of Völlmer.<sup>3</sup> The others were taken from the preceding tables.

TABLE 34. —  $\frac{a}{x}$  for potassium and sodium iodides in water and methyl and ethyl alcohols at 25°.

	H <sub>2</sub> O $x = 3.68$ constant.	CH <sub>3</sub> OH $x = 3.43$ constant.	C <sub>2</sub> H <sub>5</sub> OH $x = 2.74$ constant.
KI . . . . .	24.9	25.3	24.9
NaI ( $v = 32, 64, 100$ ) . . .	23.5	23.7	23.6
( $v = 64, 128$ ) . . . . .	24.5	25.1	...
KBr ( $v = 128, 256$ ) . . . .	25.8	26.2	...

Similarly, assuming that Dutoit and Aston's hypothesis holds for 50 per cent methyl alcohol, we may calculate the degree of association. Taking the

<sup>1</sup> Compt. rend., 125, 240 (1897).

<sup>2</sup> Ztschr. phys. Chem., 12, 433 (1893).

<sup>3</sup> Wied. Ann., 52, 328 (1894).

value of the constant as 23.6 and the comparable volume for the mixture as 48, from the relation  $\frac{a}{x} = 23.6$  we can find  $x$ . We have  $\frac{93.7}{x} = 23.6$ , whence  $x = 3.96$ .

A mixture of methyl alcohol and water, containing 50 per cent methyl alcohol by volume, has very approximately the composition corresponding to the hydrate  $\text{CH}_3\text{OH} \cdot 3 \text{H}_2\text{O}$ . The existence of alcoholic hydrates has been made probable on other grounds.

*It is possible that such hydrates, in virtue of their complexity, have high dissociating power. The greater dissociation found in the 50 per cent mixture may be due to this hydrate, in which four simple molecules combine to form a complex molecule.*

#### CAUSE OF THE MINIMUM.

The first observers of the conductivity minimum, Zelinsky and Krapiwın, offered no satisfactory explanation of it. They suggested that it might be connected with the formation of hydrates of methyl alcohol. Further than this they did not go. Jones and Lindsay would explain the existence of the minimum as due to the effect of one associated solvent on the association of another associated solvent (see p. 41).

The explanation offered by Jones and Lindsay was later strengthened by an investigation by Jones and Murray. They showed, from a study of the freezing-points of solutions of acetic and formic acids, and water—acetic acid in formic acid, formic acid in acetic acid, acetic acid in water, etc.—that the association of one solvent is apparently diminished by the presence of another associated solvent.

According to the explanation offered by Jones and Lindsay, the chief cause producing the minimum is a diminution of the dissociation of the dissolved substance, due to a diminution of the association of the solvents, and, consequently, a decrease in conductivity. We have shown that, in the 50 per cent mixture of methyl alcohol and water, the dissociation, instead of being diminished by the presence of the alcohol (or by bringing together water and the alcohol), is actually increased. This fact alone makes it evident that the explanation offered by Jones and Lindsay does not account wholly for the phenomenon.

Two factors determine conductivity—amount of dissociation and ionic mobility. Decrease in one or both of these produces decrease in conductivity. It has been shown that the decrease in conductivity in question can not be due alone to decrease in dissociation. The inevitable conclusion is, then, that it is due to a decrease in ionic mobility.

A complete explanation of the minimum in conductivity will have to account for the following facts:

- (1) The effect itself.

(2) The fact that the effect is more pronounced at a lower temperature than at a higher.

(3) The fact that rise in temperature (and in some cases increase in concentration) shifts the minimum towards a mixture containing a larger per cent of alcohol.

There is a close connection between the viscosity or fluidity of a solvent and the conductivity of electrolytes when dissolved in that solvent. The greater the fluidity, or the less the viscosity, other things being equal, the greater is the conductivity. This close relationship is shown by the fact that for certain aqueous solutions the temperature coefficients of conductivity and of fluidity are identical.

The connection between conductivity and fluidity, or viscosity, will be considered in detail in the concluding part of this section.

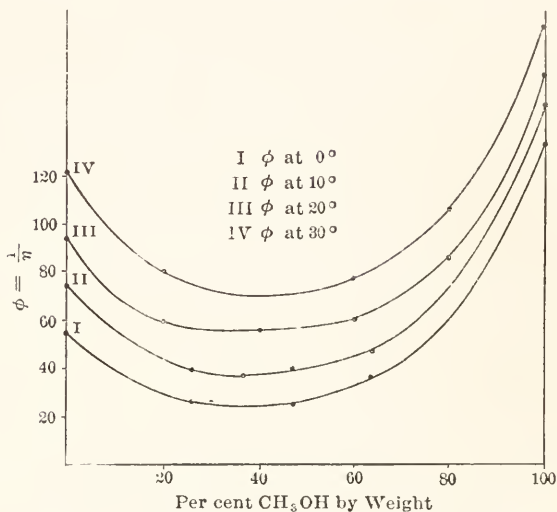


FIG. 13.—FLUIDITY OF METHYL ALCOHOL AND WATER MIXTURES.

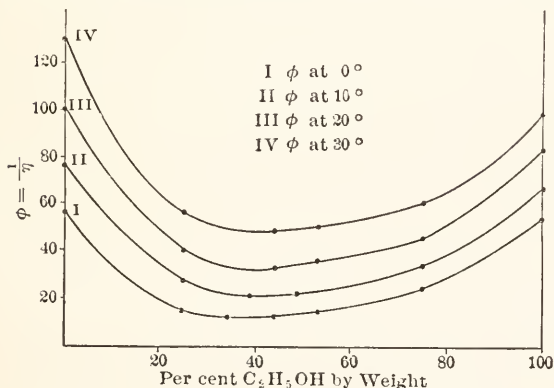


FIG. 14.—FLUIDITY OF ETHYL ALCOHOL AND WATER MIXTURES.

The investigations of Jones and Lindsay, Zelinsky and Krapiw, and this investigation have had to do with conductivities in mixtures of solvents. Numerous researches have been made on the viscosities of mixtures of liquids, notably by Graham,<sup>1</sup> Noack,<sup>2</sup> Pagliani and Battelli,<sup>3</sup> and Traube.<sup>4</sup> All of these workers have found that, in the case of mixtures of various alcohols and water,

<sup>1</sup> Lieb. Ann. **120**, 90 (1861).

<sup>2</sup> Wied. Ann., **27**, 289 (1886).

<sup>3</sup> Atti di R. Ac. delle Sc. d. Torino., **20**, 607 (1885).

<sup>4</sup> Ber. d. chem. Gesell., **19**, 871 (1889).

the *viscosity of the mixture is much greater* than would be expected from the law of averages. This is best shown graphically by plotting the viscosities as ordinates and the percentage composition of the mixtures as abscissæ. The viscosity curve is seen to pass through a maximum. The fluidity of a liquid is the reciprocal of its viscosity. If, therefore, we show graphically the variations in fluidity as the variations in viscosity were shown, the fluidity curve is seen to pass through a minimum. In all cases, of course, the fluidity is less than a proper average.

The mixtures in which the minimum of conductivity is found to occur are approximately the mixtures in which this minimum of fluidity appears. The explanation of the conductivity minimum which we offer, to supplement that suggested by Jones and Lindsay, is the following:

*The minimum in conductivity is caused primarily by the great decrease of fluidity resulting when the two components of the solvent mixture are brought together.*

From the results of Pagliani and Battelli<sup>1</sup> and of Traube<sup>1</sup> we have calculated the various fluidities of mixtures of methyl and ethyl alcohols and water, for the temperatures 0°, 10°, 20°, and 30°, and have plotted the fluidity curves (figs. 13 and 14) in the manner indicated.

A consideration of these curves makes it evident that, for mixtures of water and methyl alcohol at 0°, the minimum of fluidity occurs in a mixture containing 31 per cent methyl alcohol by weight (37 per cent by volume); at 20° the minimum occurs in a 40 per cent mixture (46 per cent by volume). Further, the drop in fluidity is more pronounced the lower the temperature.

For mixtures of ethyl alcohol and water, at 0°, the minimum occurs in a 34 per cent (40 per cent by volume) mixture. At 30° it is found in a 50 per cent (56 per cent by volume) mixture. The minimum is also more pronounced at the lower temperature.

It should be noted that the change in fluidity is very small over a considerable range — particularly in the case of mixtures of ethyl alcohol and water. At 30° the change of fluidity between 30 per cent and 60 per cent is very slight.

We have here, then, a satisfactory explanation of the minimum. The two minima, conductivity and fluidity, are parallel throughout.

The parallelism may be summed up as follows:

- (1) The conductivity minimum is found to be accompanied by a minimum in fluidity.
- (2) Both minima are more pronounced at lower temperatures, and both occur at approximately the same points.
- (3) The effect of increase in temperature is the same upon both minima —

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<sup>1</sup> Loc. cit.

there is a shifting towards a mixture containing a greater per cent of alcohol, but the fluidity minimum, so to speak, lags behind the conductivity minimum.

For comparison, table 35 is taken from the work of Jones and Lindsay.

TABLE 35. — Comparison of the molecular conductivity of potassium iodide in water, methyl alcohol, and mixtures of these solvents.

$\nu$	At 0°.						
	0 p. ct.	20 p. ct.	40 p. ct.	50 p. ct.	65 p. ct.	80 p. ct.	100 p. ct. CH <sub>3</sub> OH.
64	74.09	....	35.48	33.73	35.12	39.03	59.32
128	76.41	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.83	67.73
512	78.01	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.96	49.07	37.85	36.76	37.75	44.45	71.23
$\nu$	At 25°.						
	0 p. ct.	20 p. ct.	40 p. ct.	50 p. ct.	65 p. ct.	80 p. ct.	100 p. ct. CH <sub>3</sub> OH.
64	132.1	91.91	72.14	67.46	65.04	67.78	82.87
128	135.4	93.78	73.69	68.79	67.25	70.33	88.49
256	138.0	95.64	75.14	70.37	68.78	71.83	93.73
512	139.6	97.12	76.25	71.72	70.00	73.16	98.36
1024	140.7	98.10	77.68	72.57	70.94	74.81	102.00

It is seen that at 0° the minimum of conductivity occurs in a 50 per cent mixture; the fluidity minimum occurs in a 40 per cent mixture. At 25° the minima occur in 65 per cent and 56 per cent mixtures, respectively.

Strontium iodide also presents a good example of the shifting of the minimum, as is shown by table 36, from the work of Jones and Lindsay.

TABLE 36. — Comparison of the molecular conductivity of strontium iodide in water, methyl alcohol, and mixtures of these solvents.

$\nu$	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH.
32	113.1	63.00	50.19	55.53	75.82	205.3	131.3	103.8	98.09	101.4
64	117.7	66.05	52.61	59.24	85.01	214.5	138.5	109.9	104.8	115.3
128	122.1	68.62	55.05	62.85	94.76	223.1	145.3	115.3	111.4	128.6
256	126.0	70.98	57.18	66.68	104.4	231.8	152.3	120.1	118.0	141.4
512	129.8	73.10	59.51	69.98	114.0	240.2	157.4	124.3	124.8	153.9
1024	132.6	75.51	61.03	73.22	123.4	245.9	161.9	128.5	131.4	166.3

In the case of strontium iodide the real minimum would probably be found in a mixture between the 50 and 75 per cent mixtures. So, also, in the case of lithium nitrate, as is shown in table 37, taken from the work of Jones and Lindsay.

TABLE 37. — Comparison of the molecular conductivity of lithium nitrate in methyl alcohol, water, and mixtures of these solvents.

<i>v</i>	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH
32	50.00	29.15	23.59	26.67	45.97	91.83	60.56	47.87	47.06	63.51
64	51.49	29.68	24.49	27.95	50.12	94.62	62.16	49.92	49.52	69.32
128	52.51	30.15	25.03	28.66	53.95	98.00	63.77	51.50	51.64	74.51
256	53.40	30.70	25.71	29.51	56.67	99.68	64.96	53.57	54.36	80.57
512	54.70	31.35	26.35	30.64	60.06	101.3	66.78	54.62	56.68	83.31
1024	55.30	32.56	27.35	31.91	63.40	102.3	69.02	55.60	58.56	86.46

An examination of our own values for sodium iodide shows that at 0° the minimum occurs in the 50 per cent mixture. At 25°, for one dilution,  $v = 32$ ; it occurs in the 75 per cent mixture; elsewhere, in the 50 per cent mixture. In all probability the real minimum would be found in an intermediate mixture. When we attempt a comparison for ethyl alcohol, the data are more meager. The minimum was found by Jones and Lindsay to occur only at 0°, in the cases studied by them. Their data are given in table 38.

TABLE 38. — Comparison of the molecular conductivity of ammonium bromide, potassium iodide, and lithium nitrate.

<i>v</i>	Ammonium bromide in water, ethyl alcohol, and a 50 p. ct. mixture of these solvents at 0°.			Potassium iodide in ethyl alcohol, water, and a 50 p. ct. mixture of these solvents at 0°.			Lithium nitrate in water, a 50 p. ct. mixture with ethyl alcohol, and alcohol, at 0°.		
	H <sub>2</sub> O $\mu_r 0^\circ$	Mixture. $\mu_r 0^\circ$	C <sub>2</sub> H <sub>5</sub> OH $\mu_r 0^\circ$	H <sub>2</sub> O $\mu_r 0^\circ$	Mixture. $\mu_r 0^\circ$	C <sub>2</sub> H <sub>5</sub> OH $\mu_r 0^\circ$	H <sub>2</sub> O $\mu_r 0^\circ$	Mixture. $\mu_r 0^\circ$	C <sub>2</sub> H <sub>5</sub> OH $\mu_r 0^\circ$
32	.....	.....	.....	.....	.....	.....	50.0	13.10	14.29
64	74.22	19.42	16.71	74.09	19.26	19.12	51.49	13.56	15.60
128	75.23	19.89	18.83	76.40	19.82	21.36	52.51	14.27	17.52
256	76.62	20.09	19.66	77.01	20.35	22.66	53.40	14.63	19.39
512	77.49	20.70	22.66	78.00	20.92	25.00	54.70	15.45	21.36
1024	77.78	21.50	22.88	77.96	21.43	27.43	55.30	16.25	23.29

An examination of the data in table 38 shows that the apparent minimum occurs in a 50 per cent mixture. The fluidity minimum occurs in a 40 per cent mixture.

Jones and Lindsay also made some measurements in mixtures of methyl and ethyl alcohols. No minimum was observed, the conductivities found being about what would be expected from the rule of averages. This is clearly due to the fact that, when these two solvents are brought together, they do not exhibit the same phenomenon as is shown in the case of mixtures of the alcohols and water. We have not found any satisfactory data relative to the fluidity of mixtures of methyl and ethyl alcohols. Arrhenius<sup>1</sup> states that there is no striking change when the two are brought together.

<sup>1</sup> Ztschr. phys. Chem., 1, 287 (1887).



The best method, however, of comparing the variation in conductivity and in fluidity is not by a direct discussion of the conductivity and fluidity curves; it is better to compare the respective ratios of decrease (by per cent) of the two — that is, the differences in per cent from what would be expected from the rule of averages. These average values may be found graphically as follows: At the extremities of a straight line of chosen length erect perpendiculars proportional in length to the respective conductivities (or fluidities) of the two components of the mixtures, and connect these by a straight line. Divide the base line into parts proportional to the composition of the various mixtures. The perpendiculars joining these points of division and the line previously drawn, will be proportional in length to the various average conductivities (or fluidities). This can best be done by the use of coördinate paper. The foregoing method has been used in making the comparisons shown in table 39, from which it is seen that the variation in fluidity is in all cases greater than the variation in conductivity. The two variations must be compared in order to see where the effect of variation of fluidity is greatest. If the two effects were exactly equal,  $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$  would equal zero. In this relation we have a means of comparing the two effects. We have made the comparison in table 40.

TABLE 39. — Variation ( $\Delta\mu_v$ ) in conductivity (percentage fall in conductivity) of potassium iodide in mixtures of ethyl alcohol and water at 18°.<sup>1</sup>

<i>v</i>	20 p. ct. $\Delta\mu_v$	40 p. ct. $\Delta\mu_v$	60 p. ct. $\Delta\mu_v$	80 p. ct. C <sub>2</sub> H <sub>5</sub> OH by volume. $\Delta\mu_v$
128	0.329	0.465	0.443	0.308
256	.334	.472	.450	.311
512	.340	.481	.463	.334
1024	.339	.483	.464	.344
2048	.340	.482	.464	.343
Variation in fluidity $\Delta\phi$	.461	.627	.601	.466

<sup>1</sup> The conductivity data are taken from the work of Cohen (loc. cit.).

TABLE 40. — Comparison of variations in conductivity and in fluidity.

<i>v</i>	20 p. ct. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	40 p. ct. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	60 p. ct. $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	80 p. ct. C <sub>2</sub> H <sub>5</sub> OH $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$
128	0.287	0.258	0.263	0.339
256	.282	.247	.258	.333
512	.239	.231	.232	.283
1024	.239	.231	.232	.262
2048	.239	.231	.232	.262

It is evident that the effect of variation of fluidity on conductivity is greatest in the 40 per cent mixture, for here the values of the quotients are least. It is seen that the effect increases with increasing dilution, and finally becomes constant.

Similar comparisons are given for potassium iodide in mixtures of methyl alcohol and water at 0° and at 25°, using the results of Jones and Lindsay.

TABLE 41. — *Variation (percentage fall) in conductivity.*

<i>v</i>	Potassium iodide in mixtures of methyl alcohol and water at 0° and at 25°.									
	20 p. ct. $\Delta\mu_v$		40 p. ct. $\Delta\mu_v$		50 p. ct. $\Delta\mu_v$		65 p. ct. $\Delta\mu_v$		80 p. ct. CH <sub>3</sub> OH $\Delta\mu_v$	
	0°	25°	0°	25°	0°	25°	0°	25°	0°	25°
64	....	0.237	0.479	0.356	0.494	0.372	0.456	0.350	....	0.267
128	0.361	.257	.507	.368	.510	.386	.478	.360	....	.283
256	.365	.262	.509	.377	.502	.394	.486	.371	....	.300
512	.366	.262	.510	.379	.513	.399	.489	.381	....	.313
1024	.361	.262	.503	.379	.508	.402	.490	.386	....	.320
	.543		.695		.695		.682			

<i>v</i>	Lithium nitrate in mixtures of methyl alcohol and water at 0° and 25° (from Jones and Lindsay's data).						Sodium iodide in mixtures of methyl alcohol and water at 0° and 25°.					
	25 p. ct. $\Delta\mu_v$		50 p. ct. $\Delta\mu_v$		75 p. ct. CH <sub>3</sub> OH $\Delta\mu_v$		25 p. ct. $\Delta\mu_v$		50 p. ct. $\Delta\mu_v$		75 p. ct. CH <sub>3</sub> OH $\Delta\mu_v$	
	0°	25°	0°	25°	0°	25°	0°	25°	0°	25°	0°	25°
32	0.406	0.285	0.508	0.384	0.432	0.333	0.400	0.277	0.485	0.357	0.411	0.298
64	.417	.296	.518	.392	.443	.345	.406	.283	.505	.378	.419	.298
128	.432	.307	.532	.403	.466	.358	.409	.297	.515	.395	.423	.318
256	.436	.314	.535	.406	.472	.362	.408	.313	.508	.395	.433	.330
512	.441	.310	.541	.408	.477	.354	.409	.321	.500	.402	.446	.333
1024	.434	.300	.541	.411	.477	.354	....	....	....	....	....	....
	.600	.456	.695	.575	.661	.481	....	....	....	....	....	....

TABLE 42. — *Comparison of variation in fluidity and in conductivity.*

<i>v</i>	Potassium iodide $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$									
	20 p. ct.		40 p. ct.		50 p. ct.		65 p. ct.		80 p. ct. CH <sub>3</sub> OH	
	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	
	0°	25°	0°	25°	0°	25°	0°	25°	0°	25°
64	....	0.354	0.311	0.309	0.289	0.304	0.331	0.329	....	0.385
128	0.335	.300	.275	.285	.266	.276	.299	.321	....	.346
256	.325	....	.268	....	.261	....	.300	....	0.309	....
512	.326	.289	.266	.264	.262	.251	.282	.281	....	.279
1024	.335	.286	.276	.264	.270	.246	.282	.272	....	.262

TABLE 42.— *Comparison of variation in fluidity and in conductivity.*—Continued.

v	Lithium nitrate $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$ , at 0° and at 25°.						Sodium iodide.					
	25 p. ct.		50 p. ct.		75 p. ct. CH <sub>3</sub> OH		25 p. ct.		50 p. ct.		75 p. ct. CH <sub>3</sub> OH.	
	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	
	0°	25°	0°	25°	0°	25°	0°	25°	0°	25°	0°	25°
32	0.323	0.375	0.269	0.332	0.345	0.308	0.333	0.392	0.302	0.379	0.378	0.384
64	.305	.351	.255	.318	.330	.283	.323	.379	.273	.343	.366	.355
128	.280	.327	.235	.300	.294	(.255)	.320	.348	.260	.318	.360	.339
256	.273	.311	.230	.294	.284	(.247)	.320	.313	.269	.313	.345	.314
512	.265	.318	.222	.290	.277	.264	.320	.296	.281	.301	.325	.308
1024	.277	(.344)	.222	.285	.277	.264	....	....	....	....	....	....

Finally, in table 43 we give a comparison of the temperature coefficients of conductivity for various electrolytes and the temperature coefficients of fluidity for the various mixtures.

The volumes were 1024 for KI, LiNO<sub>3</sub>, SrI<sub>2</sub>; 256 for NaI; 128 for CdI<sub>2</sub>; 256 for Ca(NO<sub>3</sub>)<sub>2</sub>.

The temperature coefficients for the ethyl alcohol mixtures are seen to be most nearly equal in the 65 per cent mixture for potassium iodide; for the other salts in the 50 per cent mixture. The temperature coefficients of the mixtures were calculated from Noack's data.

It is evident from table 43 that for the four salts KI, LiNO<sub>3</sub>, SrI<sub>2</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub>, in most mixtures, the quotient  $\frac{\mu_v}{\phi}$  is constant to within 10 per cent (5 per cent for LiNO<sub>3</sub>). The same is true for the mixtures of methyl alcohol and water.

TABLE 43.— *Comparison of temperature coefficients of conductivity and fluidity for various electrolytes.*

	In ethyl alcohol-water mixtures.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH
$\phi - 0^\circ$ . . . .	55.39	22.8	14.15	25.6	55.5
$\phi - 25^\circ$ . . . .	112.00	60.7	41.77	55.1	85.88
$\frac{1}{\phi_{25^\circ}} \cdot \frac{\Delta\phi}{\Delta t}$ . . . .	0.0249	0.0250	0.0264	0.0216	0.0142
$\frac{1}{\mu_{25^\circ}} \cdot \frac{\Delta\mu}{\Delta t}$ . . . .	.....	.....	.....	.....	.....
KI (v = 1024) . . . .	0.0172	.....	0.0237	.....	0.0135
LiNO <sub>3</sub> (v = 1024) . . . .	0.0184	.....	0.0251	.....	0.0138
SrI (v = 1024) . . . .	0.0272	.....	0.0247	.....	0.0199
Ca(NO <sub>3</sub> ) <sub>2</sub> (v = 256) . . . .	0.0182	0.0233	0.0245	0.0210	0.0131

TABLE 43. — Comparison of temperature coefficients of conductivity and fluidity for various electrolytes. — Continued.

	In methyl alcohol-water mixtures.					
	25 p. ct.	40 p. ct.	50 p. ct.	65 p. ct.	75 p. ct.	100 p. ct. CH <sub>3</sub> OH
$\phi - 0^\circ$ . . . .	30.6	27.0	27.8	34.5	39.75	131.3—3.8°
$\phi - 25^\circ$ . . . .	69.04	63.4	60.65	68.9	81.83	182.1—25.4°
$\frac{1}{\phi} \frac{\Delta\phi}{\Delta t}$ . . . .	0.0223	0.0230	0.0216	0.0200	0.0205	0.0123
$\frac{1}{\mu_{25^\circ}} \frac{\Delta\mu_v}{\Delta t}$ KI . . . . .	.....	0.0205	0.0197	0.0187	.....	0.0121
NaI . . . . .	0.0202	.....	0.0202	.....	0.0179	0.0117
LiNO <sub>3</sub> . . . . .	0.0211	.....	0.0203	.....	0.0182	0.0118
SrI <sub>2</sub> ( $v=256$ ) . . . . .	0.0213	.....	0.0210	.....	0.0177	0.0104
CdI <sub>2</sub> . . . . .	0.0238	.....	0.0220	.....	0.0178	.....

## DISCUSSION OF RESULTS.

The value of the quotient  $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$  is a measure of the parallelism between the two phenomena—decrease in conductivity and decrease in fluidity. If the decrease were the same in both cases, other conditions being the same, the value of the quotient would be zero. The fact that it is not zero indicates that the decrease in ionic mobility resulting from the decrease in fluidity is not proportional to the latter.

When we come to compare the effect in the case of potassium iodide in mixtures of the two alcohols and water (tables 37 and 38), it is seen that the effect of decrease of fluidity on ionic mobility is greatest in the ethyl alcohol mixtures, or the two effects are here most nearly parallel. The effect is less for potassium iodide in methyl alcohol mixtures at both temperatures of observation, 0° and 25°. It is to be remembered that we are leaving out of account possible differences of dissociation. Increase in dissociation (in the mixture) over that of the corresponding aqueous solution would diminish the effect of decrease in fluidity. Apparently, this possible change in dissociation can not be very great, as some of our measurements show. A far greater and entirely impossible change in dissociation would be necessary to account for the difference in the two effects.

The minimum is much more pronounced in the methyl alcohol mixtures. It occurs, however, in the ethyl alcohol mixtures generally at 0°, but is not very marked. We have just seen that the real effect is greater in the latter case, when we make a proper comparison. The reason why it is not so evident in the case of the ethyl alcohol mixtures is to be found in the small conductivities in ethyl alcohol; these, in turn, as will be shown in the last part of this section, being small, on account of the relatively great viscosity of ethyl alcohol and its rather small dissociating power. On the other hand,

the phenomenon does exhibit itself in the other mixtures, and this is because of the high conductivities in methyl alcohol, these being high on account of the small viscosity of methyl alcohol and its relatively great dissociating power.

Considering all of the salts in the various mixtures, it is seen that, in general, the effect of increased viscosity on conductivity is greatest in that mixture in which the minimum in conductivity occurs. In some cases the maximum effect occurs elsewhere. For example, for lithium nitrate (table 40) at 25° the maximum effect is in the 75 per cent mixture, while the minimum in conductivity occurs for the most part in the 50 per cent mixture.

The explanation of this is found in the fact that, although in the one mixture the effect is greater, it is offset by the effect of the smaller fluidity of the other mixture — that of the 75 per cent mixture being 81.8, and that of the 50 per cent mixture being only 68.9. In cases where the minimum shifts with increase in dilution, the probable explanation is to be found in variation in increase of dissociation accompanying further dilution.

The result of variation in the temperature is also shown in the tables — particularly in the case of the lithium salt (table 40). At 0° the maximum effect is in the 50 per cent mixture; at 25°, in the 75 per cent mixture.

In table 43 is given a comparison of the temperature coefficients of fluidity and of conductivity for various electrolytes in the various mixtures of methyl alcohol and water, and also for ethyl alcohol mixtures, for which the data are more meager.

From table 43 it is evident that the temperature coefficients of conductivity and fluidity do not differ markedly, particularly for some salts. For potassium iodide they are most nearly equal in the 65 per cent mixture, differing by only 7 per cent. For the other salts in the 50 per cent mixture the agreement is closest, and the differences are in no cases greater than for potassium iodide in the 65 per cent mixture. In some instances the agreement is seen to be much closer (SrI<sub>2</sub>, CdI<sub>2</sub>).

For the ethyl alcohol mixture of 50 per cent, the temperature coefficients differ to about the same degree as in the methyl alcohol mixtures. In other words,  $\frac{\mu_v}{\phi} = \text{constant}$ .

These facts are significant, as will appear from the latter part of this section.

The conclusion which can be drawn is, then, *that the decrease in conductivity of electrolytes in binary mixtures of various alcohols and water, which is in some cases accompanied by the minimum conductivity observed by Zelinsky and Krapivin, Jones and Lindsay, and ourselves, is caused primarily by a diminution in the fluidity of the solvent, and a consequent decrease in ionic mobility, and secondarily by the effect of one associated solvent on the association of another such solvent.*

## VISCOSITY AND CONDUCTIVITY.

The viscosity of a liquid or solution is defined as being the force (in dynes) necessary to move a layer of the liquid or solution one molecule in thickness, and of unit area (1 sq. cm.) over another layer of the liquid, with unit velocity (1 cm. per sec.). The symbol  $\eta$  is used for the coefficient of viscosity. The fluidity of a liquid is the reciprocal of its viscosity  $= \frac{1}{\eta}$ .

It is plain that the hypothesis of Dutoit and Aston does not go very deeply into the phenomena; all that it asserts is that there is a parallelism between the amount of dissociation effected by the solvent and the amount of its own association. The Thomson-Nernst hypothesis, however, offers an explanation of more profound significance.

Dutoit and Friderich<sup>1</sup> make an attempt to find a connection between conductivity, viscosity, and association, and thus take a step in the direction of a more general hypothesis. From a study of the conductivities of solutions of different electrolytes in different solvents they came to the following conclusion:

The values of  $\mu\infty$  for a given electrolyte dissolved in different solvents are a direct function of the degree of polymerization of the solvents, and an indirect function of the coefficient of viscosity of these solvents.

The relation was found to hold only in a general way — indeed, hardly more than qualitatively.

When we come to consider the proposed relation, it is difficult to see why it should exist; it is wholly empirical, and it is not in accord with the hypothesis of Dutoit and Aston; for when complete dissociation is reached the association of the solvent is no longer an influencing factor. It is superfluous to discuss the matter further because, as stated, the relation does not hold quantitatively.

This will suffice to indicate what has thus far been done to show a connection between conductivity and viscosity. The relations hitherto brought to light are qualitative. Of far more importance is the establishment of a quantitative relationship. We shall show that such does exist, and propose the following hypothesis:

*The conductivities of comparable, equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohols, other alcohols of the same series, acetone, etc.) are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factor of the solvent. In case the hypothesis of Dutoit and Aston does not hold for the solvent in question, for "association factor of the solvent" must be substituted "amount of dissociation of the solution."*

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<sup>1</sup> Bull. Soc. Chim., [3] 19, 321 (1898).

Formulated, the hypothesis is expressed by the relation  $\frac{\mu_v \eta}{x} = \text{constant}$ , or  $\frac{\mu_v \eta}{a} = \text{constant}$ , where the symbols have the usual significance. This becomes, when  $\mu_v = \mu_\infty$ ,  $\mu_v \eta = \text{constant}$ .

The meaning of the term "comparable equivalent solutions" needs to be defined. In comparing aqueous solutions those of the same normality (containing equal gram-molecules of electrolyte in equal volumes) are strictly comparable. It is evident that this is not the case when, for example, we come to compare solutions of the same electrolyte in different solvents. In order to be strictly comparable, the solutions must contain the same number of gram-molecules of electrolyte dissolved in the same number of gram-molecules of the different solvents, or equal weights of the (same) electrolyte dissolved in volumes of the solvents which are proportional to the molecular volumes of the solvents in question. It is obvious that this is the only proper basis of comparison.

To illustrate, comparable solutions in water and in methyl alcohol would be those containing the same weight of electrolyte dissolved in 18 volumes of water and 40 volumes of methyl alcohol, because the molecular volume of water is 18, and that of methyl alcohol approximately 40. The volumes compared should always be in the ratio 18 (of water) to 40 (of methyl alcohol). Similarly, in the case of methyl and ethyl alcohols, the volumes would be as 40 to 57.5.

In the first place we have plotted (fig. 15) the variation in the fluidity of methyl and ethyl alcohols with temperature, making the different fluidities ordinates and the different temperatures abscissæ. Plotted with these, for the sake of comparison, are the conductivities of various binary electrolytes

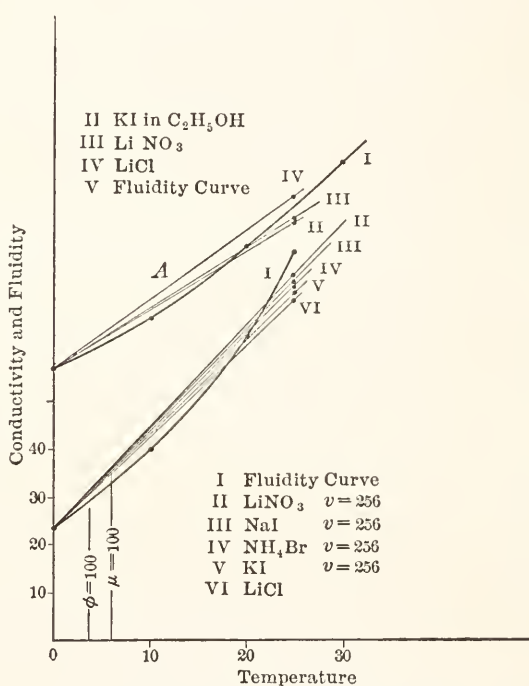


FIG. 15.—COMPARISON OF CONDUCTIVITY AND FLUIDITY.

in solution in the two solvents. Since only two observations were made, one at 0° and the other at 25°, the variation in conductivity is shown by a straight line. If observations at intermediate points could be obtained, the line would probably be curved. The first ordinate — that at 0° — is made the same in both cases. The second in the case of the conductivities is then found from the observed value by multiplication by a factor.

From an inspection of fig. 15 it is evident that the lines representing variation of conductivity and variation of fluidity with temperature are almost coincident. That is, the temperature coefficients are almost the same in both, the difference never being over 8 per cent, and in most cases much less than this, particularly for solutions in ethyl alcohol. Völlmer has already called attention to this fact. This amounts, then, to a proof of the Kohlrausch hypothesis for solutions in methyl and ethyl alcohols, and such proof is necessary to establish the validity of the one proposed.

It has already been shown that this is also true for certain electrolytes in certain mixtures of solvents. Though the temperature coefficients of fluidity and conductivity are the same, the value of the quotient  $\frac{\mu_v \eta}{\alpha}$  is much greater for an electrolyte in the mixture than for the same electrolyte in the pure alcohol. It is difficult to see why this is the case, unless it be that in the mixture we have a complex solvent not to be compared with the simple one. Certainly the presence of compounds in the mixture would complicate matters. This interesting point needs further investigation.

Knowing the values of the constant for the pure solvent, and assuming the validity of the relation for the mixture, we might calculate the ionic friction. This would not be the same as the coefficient of viscosity of the mixture, but its variation with temperature would be identical with that of conductivity.

The next step is the discussion of certain data as to conductivities in the two solvents — proof that the expression  $\frac{\mu_v \eta}{x}$  holds for solutions in these solvents. The values for the coefficients of viscosity have for the most part been taken directly, or interpolated from the results of Thorpe and Rodger.<sup>1</sup>

The values for the conductivities in the various solvents are taken from observations of Völlmer,<sup>2</sup> Carrara,<sup>2</sup> Jones and Lindsay,<sup>2</sup> and others, and from our own.

The values for the association factors are those given by Ramsay and Shields in their first paper,<sup>3</sup> at ordinary temperatures for methyl alcohol 3.43, for ethyl alcohol 2.74.

<sup>1</sup> Phil. Trans., **185A**, 397 (1894).

<sup>2</sup> Ztschr. phys. Chem., **12**, 433 (1893).

<sup>3</sup> Loc. cit.



TABLE 44.— $\frac{\mu_v\eta}{x}$  in methyl and ethyl alcohols.

For lithium nitrate.						For ammonium bromide. <sup>1</sup>	
CH <sub>3</sub> OH			C <sub>2</sub> H <sub>5</sub> OH			CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH
Volume.	0°	25°	Volume.	0°	25°	25°	0°
128	0.1288	0.1238	191	0.1239	0.1211	0.1369	0.1293
256	.1353	.1339	381	.1368	.1323	.1441	.1416
512	.1484	.1385	763	.1500	.1402	.1513	.1531

For potassium iodide.							
Volume.	CH <sub>3</sub> OH	CH <sub>3</sub> OH	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	$\frac{\mu_v\eta}{a}$	$\frac{\mu_v\eta}{a}$
	25° (Jones & Lindsay).	25° (Carrara).	0° (Jones & Lindsay).	25° (Jones & Lindsay).	0° (Jones & Lindsay).	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH
I	0.1377	0.1308	0.1417	0.1298	0.1359	0.516	0.571
II	.1471	.1408	.1526	.1428	.1479	.525	...
III	.1558	.1466	.1617	.1544	.1592	.539	.571
IV	.1636	.1513	.1665	.1698	.1760	.539	.571

<sup>1</sup> The volumes of comparison are the same as those in the case of lithium nitrate.

The conductivities compared were, for the volumes 128, 256, 512 for methyl alcohol, 190.7, 381.4, 762.8 for ethyl alcohol, these being comparable dilutions. In the case of solutions in ethyl alcohol values for the conductivities were found by interpolation.

As is seen from inspection of table 44, the constants for the comparable volumes are equal to within a few per cent. Further, the constant is the same at the lower and at the higher temperature. Of course the constants are not the same for the different volumes, for here we have used the association factor as a constant in the equation; it represents dissociation. If we were to substitute per cent of dissociation for the association factor, the values for the constant would be the same in all cases.

All together, the agreement of theory and fact is all that could be expected, when we consider the errors involved in the determination of the quantities used. The figures for association are certainly only approximate. Conductivities are liable to an appreciable error, and different observers give values for the viscosity coefficients differing by as much as 4 or 5 per cent.

Values for the conductivities in ethyl alcohol are taken from the work of Jones and Lindsay; those given by them for methyl alcohol solutions are not used. Those of Carrara are taken, as they agree with values given by Zelinsky and Krapiwın, while those of Jones and Lindsay do not.

In all the cases the agreement is as close as could be expected.

The volumes compared were 64, 128, 256, and 512 for methyl alcohol; for ethyl alcohol, 95.7, etc. The values found by both Jones and Lindsay and

Carrara, for conductivities in methyl alcohol, were used in order to compare the results. In some cases those of the one give better agreement, in other cases those of the other, indicating that the differences are due to experimental errors.

It should be stated that in this case Gartenmeister's values for the coefficients of viscosity were used. The calculations were made before it was decided to use those given by Thorpe and Rodger. It would hardly be profitable to recalculate, since the result is the same whichever set of values be employed. We have satisfied ourselves of this by numerous trials. In many cases three or four calculations were made, using the different constants given in the tables of Landolt and Börnstein.

TABLE 45. —  $\frac{\mu_v \eta}{x}$  for lithium chloride in methyl, ethyl, and propyl alcohols.

CH <sub>3</sub> OH, 25° . . . . .	0.1213 .1166	Völlmer—18°
C <sub>2</sub> H <sub>5</sub> OH, 18° . . . . .	.1256	
C <sub>3</sub> H <sub>7</sub> OH, 15° . . . . .	.1164	

The volumes compared in table 45 are 256, 403, 604. The values for the conductivities are taken from the work of Carrara and Völlmer, and for *n*-propyl alcohol from Schlamp.<sup>1</sup> The agreement is satisfactory.

It is interesting to note that the relation holds for picric acid in solution in methyl and ethyl alcohols. Where the volumes compared are 205 and 270, respectively,  $\frac{\mu_v \eta}{x}$  in the one case equals 0.0665, and in the other, 0.0641. The data for the comparison are furnished by Schall.<sup>2</sup>

Other results may be summarized (table 46) without further detail. In all the instances given the agreement continues to be satisfactory.

TABLE 46. —  $\frac{\mu_v \eta}{x}$  for various electrolytes in different solvents.

	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	
NaI . . . . .	0.1438	0.1447	.....	{ Jones & Carroll (25°). Völlmer (18°).
<i>v</i> = 200, 283 . . . . .	.....	.....	.....	
<i>v</i> = 750, 575 . . . . .	.157	.....	0.159	{ Jones & Carroll (25°). Schlamp (15°).
CH <sub>3</sub> COONa . . . . .	.1156	.....	.....	Völlmer (18°).
<i>v</i> = 832, 1200 . . . . .	.1123	.1093	.....	Carrara (25°); Völlmer (18°).
CH <sub>3</sub> COOK NaCl . . . . .	.1279	.1247	.....	Völlmer (18°).
<i>v</i> = 228, 340 . . . . .	.1457	.1366	.....	Carrara (25°); Völlmer (18°).

<sup>1</sup> Landolt und Börnstein's Tabellen.

<sup>2</sup> Ztschr. phys. Chem., 14, 707 (1894).

In the foregoing pages we have discussed all the material available in the literature. In all of the cases — some nine in number — fact and theory are in accord. It can, therefore, be fairly claimed that the proposed hypothesis becomes highly probable. Further investigation is, however, desirable, to see how widely it applies.

For solutions in which dissociation is complete the formulated hypothesis becomes  $\mu\eta = \text{constant}$ . The proof of the validity of this relation is, it seems to us, a crucial test. Table 47 gives the necessary comparisons.

TABLE 47. —  $\mu\eta$  for various electrolytes in various solvents.

Electrolyte.	$\text{C}_2\text{H}_5\text{OH}$ $n = 0.012385$ 18°	$\text{CH}_3\text{OH}$ $n = 0.00666$ (18°) 0.00552 (25°)	$\text{CH}_3\text{COCH}_3$ $n = 0.00353$ 25°	$n\text{-C}_3\text{H}_7\text{OH}$ $n = 0.002554$ 15°
KI . . . . .	0.567	0.530—18° .528—25°	0.541	....
NaI . . . . .	.466	.505—18° .496—25°	.494	0.481
$\text{NH}_4\text{I}$ . . . . .	....	.581	.538	.431
LiCl . . . . .	.377	.416—18° .427—25°	....	....
NaCl . . . . .	.434	.479	....	....

The values for acetone were taken from the work of Carrara,<sup>1</sup> those for ethyl alcohol from that of Völlmer,<sup>2</sup> those for methyl alcohol from that of Völlmer<sup>2</sup> and Carrara,<sup>2</sup> and those for propyl alcohol from the investigation of Schlamp.

When we consider the necessarily large experimental error involved in the determination of the limiting values for conductivity — an error which must certainly be greater than that involved in the determination of conductivities at ordinary dilutions — the agreement is as good as could be expected. Further, for lithium and sodium chlorides in ethyl alcohol, limiting values were probably not reached, for with them Völlmer did not go to a dilution as high as in other cases. The true values for these salts would probably be greater than the values given in the table, thus making a still better agreement.

## SUMMARY AND CONCLUSIONS.

(1) The investigations of Zelinsky and Krapiwín and of Jones and Lindsay have been extended, and the occurrence of the minimum in conductivity has been shown for three substances, cadmium iodide, sodium iodide, and hydrochloric acid, in mixtures of methyl alcohol and water.

(2) The dissociation (as determined from conductivity) of sodium and potassium iodides, and potassium bromide in 50 per cent methyl alcohol, has been determined and has been found to be greater than that in water at the corresponding dilution.

<sup>1</sup> Gazz. Chim. Ital., 27 (1), 207 (1897).<sup>2</sup> Loc. cit.

(3) It has been shown that the explanation of the minimum in conductivity offered by Jones and Lindsay is not sufficient. The phenomenon has been shown to be *dependent primarily upon the decrease in fluidity* which results when the components of the solvent are mixed.

(4) The hypothesis of Dutoit and Aston has been proved quantitatively for certain salts in three solvents — water, methyl alcohol, and ethyl alcohol.

(5) The hypothesis of Kohlrausch (formation of an atmosphere of the solvent around the ions in solution) has been shown to hold for binary electrolytes in methyl and ethyl alcohols.

(6) A hypothesis correlating conductivity, association, and viscosity (or fluidity) has been proposed, and has been shown to hold for all the cases available for discussion.

## WORK OF BASSETT.

### EXPERIMENTAL WORK.

This investigation was undertaken for the purpose of determining what effect mixtures of methyl alcohol and water would have on the relative velocities of the ions of such a salt as silver nitrate.

The work of Jones and Lindsay<sup>1</sup> on the conductivity of certain salts in water, methyl, ethyl, and propyl alcohols, and mixtures of these solvents, suggested this work.

In their work, Jones and Lindsay found that the conductivities of such salts as potassium iodide, ammonium bromide, strontium iodide, etc., were less in mixtures of the solvents than in either of the solvents alone. Especially was this the case in mixtures of methyl alcohol and water. Considering these facts, the first thing to determine was whether silver nitrate would give similar conductivity results, and if so, whether there was any relation between this phenomenon and the relative velocities. The conductivities of silver nitrate in these solvents and varying mixtures of them were determined. The water and methyl and ethyl alcohols were purified by the methods described by Jones and Lindsay. In each case a mother-solution was made in the solvent in question, and the remaining solutions were obtained by successive dilutions with some of the solvent of the same composition. In this way an error was avoided which would result from the contraction when alcohol and water were mixed, and also prevent the accompanying heat effect. In some cases, as in very dilute solutions, where such small quantities of the mother-solution were required, a second mother-solution was made from the first, and the more dilute solutions made from it in the way described. The strength of these mother-solutions was determined by titrating with a standard solution of ammonium sulphocyanate.

### CONDUCTIVITY APPARATUS EMPLOYED.

The apparatus described and used was similar to that employed by Jones and Lindsay. The cells differed from the ordinary Arrhenius cell, being provided with a ground-glass top to prevent evaporation of the more volatile solvents, and also to protect the anhydrous alcoholic solutions from the moisture of the baths and air. The glass tubes carrying the electrodes were passed through thin rubber tubes in the cap. Sealing-wax was then run over the outside of the joint.

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<sup>1</sup> Amer. Chem. Journ., 28, 329 (1902).

The zero-bath was prepared as follows: A large glass battery-jar was filled with finely crushed ice and distilled water. It was then placed in a water-bath and the space between filled with finely crushed ice and water. This proved very efficient, as it was possible to keep within  $0.05^\circ$  of zero for hours. The bath at  $25^\circ$  was of the ordinary form, and was kept in constant motion by a stirrer driven by means of a hot-air engine. The thermometers used could be accurately read to  $0.02^\circ$ . The burettes and flasks were carefully calibrated.

## CONDUCTIVITY MEASUREMENTS.

All the conductivity measurements were made at the two temperatures,  $0^\circ$  and  $25^\circ$ . In tables 48 to 50,  $v$  = number of liters of solution containing a gram-molecular weight of the salt;  $\mu_v 0^\circ$  = molecular conductivity at  $0^\circ$ ;  $\mu_v 25^\circ$  = molecular conductivity at  $25^\circ$ .

TABLE 48. — *Molecular conductivity of silver nitrate.*

$v$	In water.		$v$	In ethyl alcohol.		$v$	In methyl alcohol.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$		$\mu_v 0^\circ$	$\mu_v 25^\circ$		$\mu_v 0^\circ$	$\mu_v 25^\circ$
10	55.72	99.46	9.71	7.11	....	10	25.96	35.77
20	58.63	105.72	19.43	8.90	14.26	20	32.63	44.67
40	63.10	110.22	38.86	11.35	16.96	40	39.71	53.42
80	65.38	115.81	77.73	13.10	20.11	80	45.28	62.95
160	65.38	119.86	155.47	15.13	23.87	160	51.09	70.36
320	69.91	125.08	310.95	17.04	26.46	320	56.71	80.17
640	71.05	125.86	621.89	19.43	30.62	640	61.42	88.22
1280	70.59	125.35						

$v$	In 25 p. ct. ethyl alcohol and water.		In 50 p. ct. ethyl alcohol and water.		In 75 p. ct. ethyl alcohol and water.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
19.43	....	....	15.25	37.87	13.12	27.01
38.86	25.95	59.70	15.81	39.50	14.30	30.43
77.73	26.65	62.75	17.04	42.42	16.79	33.65
155.47	26.45	63.82	17.92	45.15	19.48	35.94
310.95	28.72	64.87	19.10	47.13	18.00	39.01
621.89	28.84	68.28	19.90	49.39	19.41	40.14
1243.78	....	....	20.79	52.80	....	....

$v$	In 25 p. ct. methyl alcohol and water.		In 50 p. ct. methyl alcohol and water.		In 75 p. ct. methyl alcohol and water.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
20	....	....	27.27	53.33	27.98	48.20
40	35.63	72.68	28.63	56.80	30.03	52.33
80	36.95	75.56	29.93	59.75	32.81	57.17
160	39.03	79.34	31.47	63.22	35.22	61.31
320	41.03	82.93	32.29	65.85	35.71	63.23
640	41.23	83.91	34.67	68.67	40.27	69.42

TABLE 49. — *Temperature coefficients of conductivity of silver nitrate.*

$\nu$	In water (0° to 25°).	In methyl alcohol (0° to 25°).	In mixtures of methyl alcohol and water of various compositions.		
			25 p. ct.	50 p. ct.	75 p. ct.
10	1.75	0.392	....	....	....
20	1.88	0.482	....	1.04	0.810
40	1.88	0.548	1.48	1.13	0.892
80	2.10	0.707	1.54	1.19	0.974
160	2.14	0.771	1.61	1.27	1.024
320	2.21	0.938	1.68	1.34	1.100
640	2.20	1.702	1.71	1.36	1.166
1280	2.19	....	....	....	....

$\nu$	In ethyl alcohol (0° to 25°).	In mixtures of ethyl alcohol and water of various compositions.		
		25 p. ct.	50 p. ct.	75 p. ct.
19.43	0.214	....	0.905	0.556
38.86	.224	1.35	0.962	.645
77.73	.280	1.44	1.015	.674
155.47	.350	1.49	1.089	.658
310.95	.377	1.45	1.121	.840
621.89	.488	1.58	1.180	.829
1243.78	....	....	1.280	....

TABLE 50. — *Comparison of the molecular conductivities of silver nitrate.*

$\nu$	In ethyl alcohol and mixtures of it with water at 25° C. and 0° C.							
	At 25° C.				At 0° C.			
	25 p. ct. alcohol.	50 p. ct. alcohol.	75 p. ct. alcohol.	100 p. ct. alcohol.	25 p. ct. alcohol.	50 p. ct. alcohol.	75 p. ct. alcohol.	100 p. ct. alcohol.
9.71	....	....	....	....	....	....	....	7.11
19.43	....	37.87	27.01	14.26	....	15.25	13.12	8.90
38.86	59.70	39.50	30.43	16.96	25.95	15.81	14.30	11.35
77.73	62.75	42.42	33.65	20.11	26.65	17.04	16.79	13.10
155.47	63.82	45.15	35.94	23.87	26.45	17.92	19.48	15.13
310.95	64.87	47.13	39.01	26.46	28.72	19.10	18.00	17.04
621.89	68.28	49.39	40.14	30.62	28.84	19.90	19.41	19.43
1243.78	....	....	....	....	....	20.79	....	....

$\nu$	In water, methyl alcohol, and mixtures of these solvents at 25° C. and 0° C.									
	At 25° C.					At 0° C.				
	Water.	25 p. ct. alcohol.	50 p. ct. alcohol.	75 p. ct. alcohol.	100 p. ct. alcohol.	Water.	25 p. ct. alcohol.	50 p. ct. alcohol.	75 p. ct. alcohol.	100 p. ct. alcohol.
10	99.46	....	....	....	35.77	55.72	....	....	....	25.96
20	105.72	....	53.33	48.20	44.67	58.63	....	27.27	27.98	32.63
40	110.22	72.68	56.80	52.33	53.42	63.10	35.63	28.63	30.03	39.71
80	115.81	75.56	59.75	57.17	62.95	63.16	36.95	29.93	32.81	45.28
160	119.86	79.34	63.22	61.31	70.36	65.38	39.03	31.47	35.22	51.09
320	125.08	82.93	65.85	63.23	80.17	69.91	41.03	32.29	35.71	56.71
640	125.86	83.91	68.67	69.42	88.22	71.05	41.23	34.67	40.27	61.42
1280	125.35	....	....	....	....	70.59	....	....	....	....

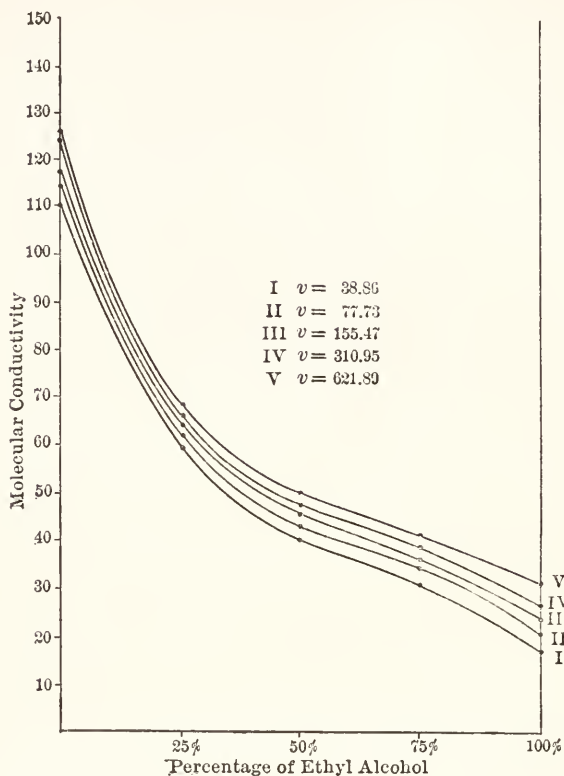


FIG. 16.—CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°.

In order to see the connection existing between the conductivities in each solvent, table 50 is given for comparison.

It is seen from the values in table 50 that the molecular conductivity in ethyl alcohol and mixtures with water does not show a minimum over the ordinary range of dilution, but still does not obey the law of mixtures. This is in accordance with the work of Jones and Lindsay on potassium iodide. In that case they did not find a trace of a minimum at 25°. The values in the first part of table 50 are plotted as curves in fig. 16, the abscissæ representing the different per cents of alcohol and the ordinates the molecular conductivities.

The curves in fig. 17 are of the same general form as those in fig. 16. No distinct minimum is shown, but the form of the curve indicates that a minimum value is approached.

In nearly every case the minimum, as shown by the curves in fig. 18,



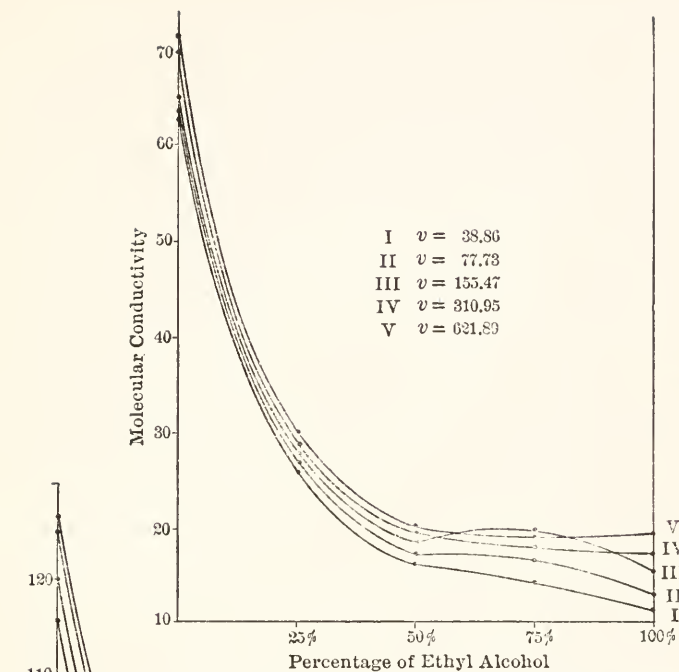


FIG. 17. — CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 0°.

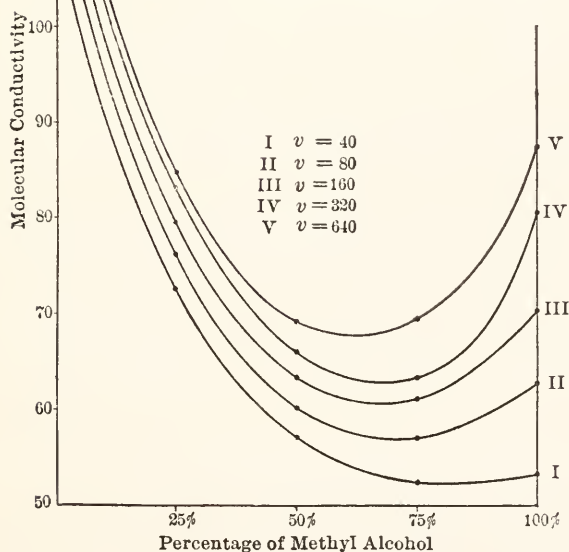


FIG. 18. — CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 25°.

lies between mixtures of the solvents containing respectively 50 and 75 per cent of alcohol.

The curves in fig. 19 are of the same general form as those in fig. 18. They differ, however, in some respects. The chief difference is that the minimum point has shifted to the left, corresponding now to an alcohol-water mixture not far from 50 per cent.

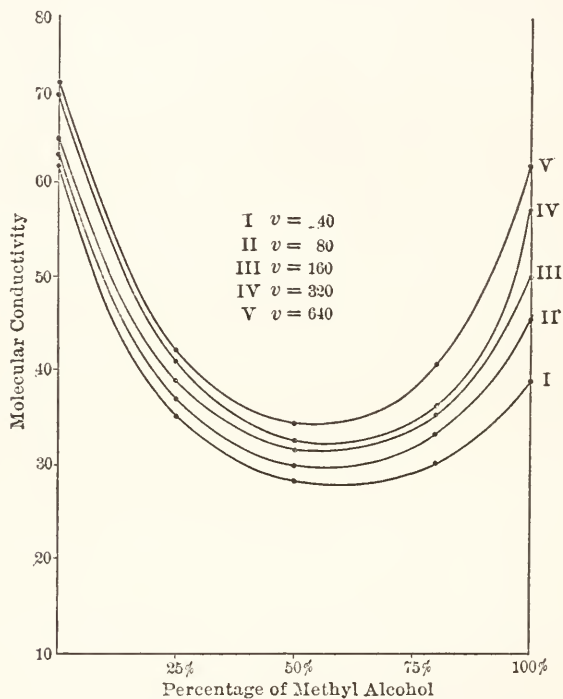


FIG. 19.—CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 0°.

From the above results it is clear that silver nitrate is not an exception to the general relation found by Jones and Lindsay.

## WORK OF BINGHAM.

### EXPERIMENTAL.

#### APPARATUS.

#### CONDUCTIVITY.

The Kohlrausch method of measuring conductivity, with Wheatstone bridge, telephone receiver, and induction coil, was employed. It was not difficult to read to less than 0.1 of 1 per cent. The bridge-wire was made of "manganin" and was calibrated before beginning the work. The resistance coils were carefully standardized.

In order to work successfully with acetone, it was necessary to provide cells of special construction, so as to avoid the presence of rubber or wax, which would be dissolved by the solutions. The cells were made of hard glass with ground-glass stoppers, and had the form shown in fig. 20. The glass tubes carrying the electrodes were sealed into both the upper and the lower walls of the glass stopper. The distance between the electrodes thus remained permanently fixed.

The zero-bath was prepared by filling a large battery-jar with clean, finely crushed ice, moistened with water. This was placed in a pail made of compressed paper pulp, and the annular space filled with finely crushed ice. Thus protected, the bath could be used for a much longer time than with the methods usually employed. The 25° bath was of the usual form, the stirrer being driven by means of a hot-air engine. An Ostwald regulator was employed. The thermometers were regulated to tenths of a degree. They were tested at the beginning of the work. Burettes and flasks were carefully calibrated.

#### VISCOSITY.

The viscometer was of the form recommended by Ostwald.<sup>1</sup> A fixed volume of the liquid to be measured was introduced into the apparatus. The

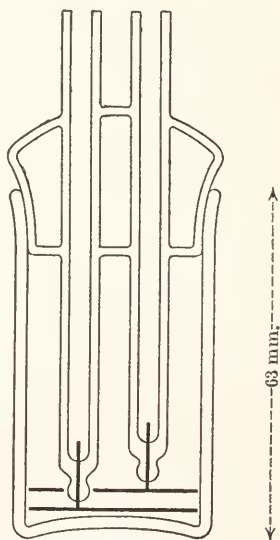


FIG. 20.

<sup>1</sup> Physiko-Chemische Messungen, 2d ed., p. 260.

liquid was raised exactly to the mark above the bulb, by air-pressure. The air was dried over sulphuric acid. The pressure was released by means of a Mohr pinchcock, on a thick-walled rubber tube. By this arrangement the readings agreed to within 0.2 of a second. It was important that the liquids should be given time to drain out of the tube above the upper mark, since, otherwise, a drop of liquid might collect in the upper capillary and impede the entering air, thus introducing large error.

For the zero-bath a battery-jar was filled with very finely crushed ice moistened with water. The ice was renewed as often as was necessary to keep the temperature constant. For the 25° bath a 5-liter beaker was employed. The bath was stirred by means of a hot-air engine, the temperature being kept to within 0.1° of 25°, as in the conductivity method. The room was kept as near this temperature as possible.

To measure the specific gravities at zero, which was necessary in order to calculate the viscosities, we constructed a pycnometer (fig. 21) which would allow the large expansion of the alcohols and acetone and avoid loss by evaporation.

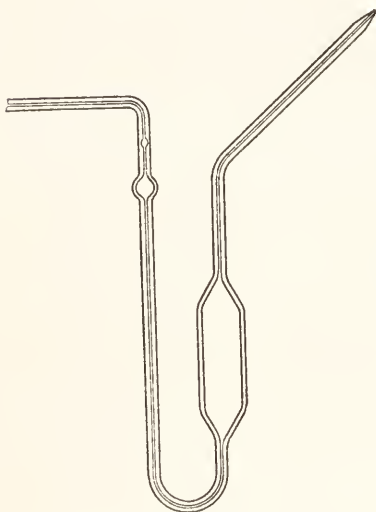


FIG. 21.

#### PREPARATION OF SOLUTIONS.

In making up mixtures of solvents, *n* c. c. of acetone diluted to 100 c. c. was designated as a mixture of "*n* per cent acetone." Since acetone, especially, has a high coefficient of expansion, it was important to have the temperature always the same, 20°. The acetone or alcohol was brought to this temperature before making up the mixture. On mixing acetone and water, contraction took place and heat was generated, so that the mixture was brought to the temperature before diluting to the mark.

The mother-solution was made by weighing into a measuring-flask the exact amount of salt required, and adding the mixed solvent. Since, however, heat was again generated, especially with the calcium nitrate, the solution was again brought to the designated temperature before diluting to the mark.

From the mother-solution the other solutions were made by successive dilutions. Where this would necessitate the use of small quantities of solution, a new mother-solution was made, and from this successive dilutions prepared.

## SOLVENTS.

## WATER.

The water was purified by the method of Jones and Mackay,<sup>1</sup> and had a conductivity of  $1 \times 10^{-6}$  at 0°.

## METHYL ALCOHOL.

The methyl alcohol was the best commercial article obtainable. It was boiled with calcium oxide for a day, distilled, and allowed to stand over anhydrous copper sulphate for a long time. Before use it was distilled, using a Linnemann fractionating head. Precautions were taken against absorption of moisture. The first and last portions of the distillate were discarded, giving a liquid which boiled constantly at 66°. The mean value of the conductivity was  $2 \times 10^{-6}$  at 25°.

## ETHYL ALCOHOL.

The ethyl alcohol was the best commercial alcohol obtainable. It was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of  $2 \times 10^{-6}$  at 25°.

## ACETONE.

The acetone was dried over fused calcium chloride for weeks and distilled with a fractionating head as above. Its conductivity was  $0.6 \times 10^{-6}$ .

## CONDUCTIVITY MEASUREMENTS.

In all determinations of conductivity at least three different resistances were used, and the values given are the mean. However, if the readings did not agree to 0.1 of 1 per cent, they were usually repeated. The constants of the cells were checked at frequent intervals. The cells were not allowed to remain in contact with the solution when not in use, nor to remain empty after being dried out with alcohol and ether. In the former case, small quantities of salt were found to be slowly absorbed, and in the latter acetic acid was formed by the action of the platinum on the alcohol or ether in the presence of air. When not in use the cells were filled with pure distilled water.

A N/50 and a N/500 solution of potassium chloride were used in determining the cell constants. The conductivity of the former was taken as 129.7 at 25°. The value of the latter was determined several times in different cells. The mean value obtained agrees well with the interpolated values of other observers.

The temperature coefficients are obtained by dividing the increase in the conductivity per degree by the conductivity at the lower temperature.

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<sup>1</sup> Ztschr. phys. Chem., **22**, 237 (1897). Amer. Chem. Journ., **19**, 91 (1897).

TABLE 51.—*Conductivity of N/500 potassium chloride at 25°.*

Observed value corrected for the conductivity of water.....	136.5
Corresponding value obtained by Jones and West <sup>1</sup> .....	135.5
Deduced value, from Kohlrausch <sup>2</sup> .....	136.94
Interpolated value, from Ostwald <sup>3</sup> .....	138.7

## LITHIUM NITRATE.

The lithium nitrate used in this work was a sample obtained from Kahlbaum. No appreciable impurity could be detected. It was dried in an air-bath at 150° until the weight remained constant. The salt was kept in a desiccator. The operation of drying was repeated whenever the salt was exposed to the air.

TABLE 52.—*Conductivity of lithium nitrate at 0° and 25°.*

<i>v</i>	In methyl alcohol.			In a mixture of 25 p. ct. acetone and methyl alcohol.			In a mixture of 50 p. ct. acetone and methyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
5	31.17	43.05	0.0154	33.50	44.27	0.0128	32.79	41.26	0.0103
10	37.62	51.31	.0145	40.78	53.85	.0128	41.11	51.68	.0100
25	43.40	60.49	.0158	48.36	64.63	.0134	51.38	65.39	.0109
50	48.31	67.2	.0157	54.29	72.8	.0136	58.82	75.42	.0113
100	52.0	72.6	.0155	58.9	79.8	.0148	65.2	84.8	.0120
200	55.1	76.8	.0147	63.6	85.9	.0140	69.6	93.2	.0135
400	56.8	80.0	.0172	66.2	90.6	.0147	75.2	99.2	.0128
800	59.6	83.7	.0162	69.8	95.7	.0148	80.0	105.3	.0127
1200	60.8	85.3	.0160	71.0	97.7	.0150	83.3	109.6	.0126
1600	61.9	86.7	.0160	73.1	99.8	.0146	86.8	112.2	.0117

<i>v</i>	In a mixture of 75 p. ct. acetone and methyl alcohol.			In acetone.			In ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
5	25.53	29.98	0.00703	7.78	9.25	0.00755	9.14	14.65	0.0241
10	34.06	39.45	.0158	9.67	10.87	.00493	10.75	17.17	.0238
25	45.86	53.69	.00683	11.35	12.86	.00532	13.55	21.71	.0240
50	55.50	66.30	.0078	14.07	15.64	.00447	15.54	24.9	.0241
100	65.2	78.4	.0081	18.1	19.5	.00310	16.9	27.6	.0251
200	74.8	92.2	.0093	23.8	25.3	.00252	18.4	30.3	.0260
400	82.6	103.0	.0099	30.6	32.4	.00232	19.1	32.1	.0271
800	90.0	113.3	.0103	43.4	45.5	.00193	20.3	34.1	.0251
1200	94.4	119.0	.0104	48.7	52.5	.00311	20.0	34.4	.0288
1600	96.6	123.6	.0112	55.3	59.8	.00325	21.7	35.4	.0252

<i>v</i>	In a mixture of 25 p. ct. acetone and ethyl alcohol.			In a mixture of 50 p. ct. acetone and ethyl alcohol.			In a mixture of 75 p. ct. acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
5	12.5	18.6	0.0195	15.2	19.7	0.0142	14.1	16.9	0.00795
10	15.9	22.9	.0176	19.6	25.4	.0119	19.3	22.5	.0066
25	20.2	29.2	.0178	26.1	33.8	.0118	27.2	31.3	.0060
50	23.1	33.9	.0187	30.9	40.4	.0123	34.3	39.7	.0063
100	26.0	38.4	.0191	35.7	47.6	.0133	41.7	49.6	.0074
200	29.0	43.2	.0196	40.4	54.8	.0142	50.2	60.1	.0079
400	31.2	46.6	.0198	44.4	61.3	.0152	54.2	70.8	.0122
800	33.0	50.3	.0210	47.4	67.0	.0165	64.9	80.9	.0098
1200	34.6	51.8	.0222	49.4	69.6	.0164	69.5	86.5	.0098
1600	35.1	54.5	.0220	50.7	71.9	.0167	70.6	91.7	.0119

<sup>1</sup> Amer. Chem. Journ., 34, 357 (1905).<sup>2</sup> Leitvermögen der Elektrolyten.<sup>3</sup> Lehrbuch der allgemeinen Chem., 2d ed., p. 732.

TABLE 52. — *Conductivity of lithium nitrate at 0° and 25°.* — Continued.

<i>v</i>	In water.			In a mixture of 25 p. ct. acetone and water.		
	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temp. coef.	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temp. coef.
5	44.45	80.72	0.0323	27.31	55.69	0.0415
10	46.39	83.87	.0323	27.37	56.35	.0421
25	49.57	91.4	.0334	30.32	62.76	.0427
50	51.4	94.4	.0334	31.50	65.3	.0430
100	52.5	97.0	.0340	32.8	70.5	.0460
200	53.1	98.8	.0342	34.1	72.5	.0450
400	54.3	100.8	.0341	34.6	76.0	.048
800	55.0	102.0	.0340	37.6	77.8	.043
1200	55.9	102.6	.0332	39.0	80.7	.0425
1600	56.3 (58.3)	102.8 (107.0)	.0330	40.0	83.1	.0430

<i>v</i>	In a mixture of 50 p. ct. acetone and water.			In a mixture of 75 p. ct. acetone and water.		
	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temp. coef.	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temp. coef.
5	21.81	43.37	0.0394	21.25	36.78	0.0292
10	23.48	47.84	.0415	24.41	42.65	.0298
25	24.90	51.33	.0425	27.64	48.92	.0308
50	26.26	54.4	.0427	30.25	54.14	.0316
100	27.2	57.3	.0442	31.8	57.4	.0322
200	29.1	60.0	.0425	33.5	61.4	.0333
400	28.8	60.0	.0433	35.1	63.6	.0325
800	29.9	62.7	.0440	36.7	66.3	.0322
1200	31.6	65.9	.0425	38.1	68.6	.0320
1600	32.3	67.5	.0435	37.8	69.1	.0331

TABLE 53. — *Comparison of the conductivities of lithium nitrate.*

<i>v</i>	In mixtures of acetone and methyl alcohol.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	31.17	33.50	32.79	25.53	7.78	43.05	44.27	41.26	29.98	9.25
10	37.62	40.78	41.11	34.06	9.67	51.31	53.85	51.68	39.45	10.87
25	43.40	48.36	51.38	45.86	11.35	60.49	64.63	65.39	53.69	12.86
50	48.31	54.29	58.82	55.50	14.07	67.2	72.8	75.42	66.30	15.64
100	52.0	58.9	65.2	65.2	18.1	72.6	79.8	84.8	78.4	19.5
200	55.1	63.6	69.6	74.8	23.8	76.8	85.9	93.2	92.2	25.3
400	56.8	66.2	75.2	82.6	30.6	80.0	90.6	99.2	103.0	32.4
800	59.6	69.8	80.0	90.0	43.4	83.7	95.7	105.3	113.3	45.5
1200	60.8	71.0	83.3	94.4	48.7	85.3	97.7	109.0	119.0	52.5
1600	61.9	73.1	86.8	96.6	55.3	86.7	99.8	112.2	123.6	59.8

<i>v</i>	In mixtures of acetone and ethyl alcohol.									
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	9.14	12.5	15.2	14.1	7.78	14.65	18.6	19.7	16.9	9.25
10	10.75	15.9	19.6	19.3	9.67	17.17	22.9	25.4	22.5	10.87
25	13.55	20.2	26.1	27.2	11.35	21.71	29.2	33.8	31.3	12.86
50	15.54	23.1	30.9	34.3	14.07	24.90	33.9	40.4	39.7	15.64
100	16.9	26.0	35.7	41.7	18.1	27.60	38.4	47.6	49.6	19.5
200	18.4	29.0	40.4	50.2	23.8	30.3	43.2	54.8	60.1	25.3
400	19.1	31.2	44.4	54.2	30.6	32.1	46.6	61.3	70.8	32.4
800	20.3	33.0	47.4	64.9	43.4	34.1	50.3	67.0	80.9	45.4
1200	20.0	34.6	49.4	69.5	48.7	34.4	51.8	69.6	86.5	52.5
1600	21.7	35.1	50.7	70.6	55.3	35.4	54.5	71.9	91.7	59.8

TABLE 53. — Comparison of the conductivities of lithium nitrate. — Continued.

$v$	In mixtures of acetone and water at 0°.					In mixtures of acetone and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	44.45	27.31	21.81	21.25	7.78	80.72	55.69	43.37	36.78	9.25
10	46.39	27.37	23.48	24.41	9.67	83.87	56.35	47.84	42.65	10.87
25	49.57	30.32	24.90	27.64	11.35	91.4	62.74	51.33	48.92	12.86
50	51.4	31.50	26.26	30.25	14.07	94.4	65.3	54.4	54.14	15.64
100	52.5	32.8	27.2	31.8	18.1	97.0	70.5	57.3	57.4	19.5
200	54.8	34.1	29.1	33.5	23.8	98.8	72.5	60.0	61.4	25.3
400	54.3	34.6	28.8	35.1	30.6	100.8	76.0	60.0	63.6	32.4
800	55.0	37.6	29.9	36.7	43.4	102.0	77.8	62.7	66.3	45.5
1200	55.9	39.0	31.6	38.1	48.7	102.6	80.7	65.9	68.6	52.5
1600	56.3	40.0	32.3	37.8	55.3	102.8	83.1	67.5	69.1	59.8

Table 53 (figs. 22 and 23) shows that lithium nitrate, in mixtures of methyl alcohol and acetone, gives a pronounced maximum in conductivity.

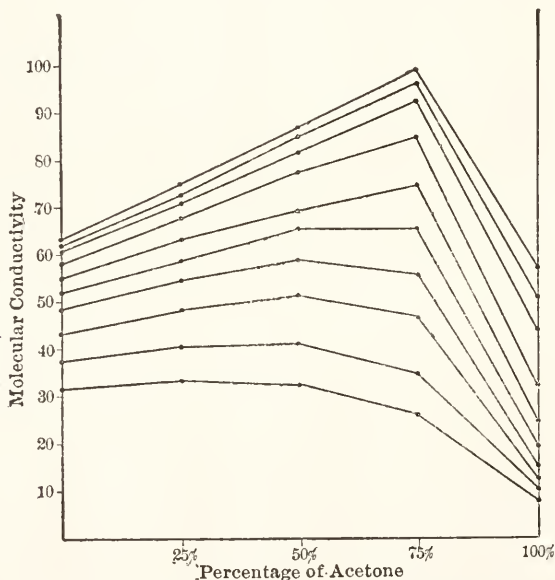


FIG. 22. — CONDUCTIVITY OF LITHIUM NITRATE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 0°.

At high concentrations the maximum is rather small. As the dilution is increased the maximum appears in the 75 per cent mixture and even beyond. It should also be noticed that, in the dilute solutions, the rise in conductivity is directly proportional to the amount of acetone, up to the 75 per cent mixture. The maximum is increased by rise in temperature.

The points will be made clear by a study of the figures. In all cases the curves represent the molecular conductivities at the successive dilutions.



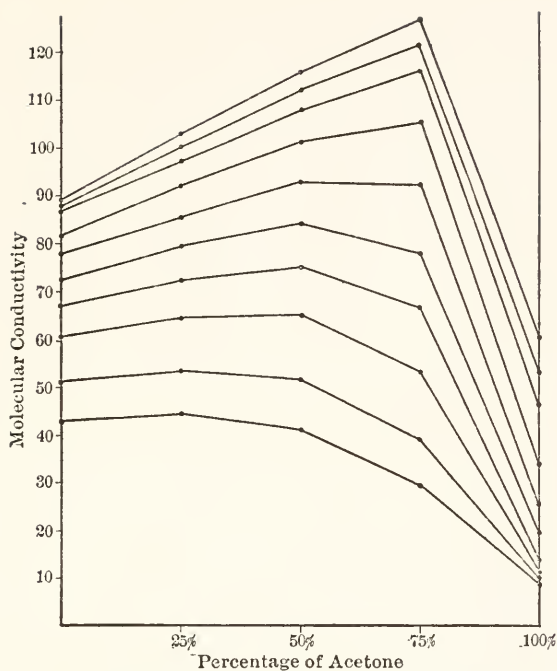


FIG. 23.—CONDUCTIVITY OF LITHIUM NITRATE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 25°.

TABLE 54.—Comparison of the temperature coefficients of conductivity of lithium nitrate.

$v$	In mixtures of acetone and methyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	0.0152	0.0129	0.0103	0.00703	0.00755
10	.0145	.0128	.0100	.00158	.00493
25	.0158	.0134	.0109	.00683	.00532
50	.0157	.0136	.0113	.0078	.00447
100	.0155	.0148	.0120	.0081	.00310
200	.0147	.0140	.0135	.0093	.00252
400	.0172	.0147	.0128	.0099	.00232
800	.0162	.0148	.0127	.0103	.00192
1200	.0160	.0150	.0126	.0104	.00311
1600	.0160	.0146	.0117	.0118	.00325
$v$	In mixtures of acetone and ethyl alcohol.				
5	0.0241	0.0195	0.0142	0.00795	0.00755
10	.0238	.0176	.0119	.0066	.00493
25	.0240	.0178	.0118	.0060	.00532
50	.0241	.0187	.0123	.0063	.00447
100	.0251	.0191	.0133	.0074	.00310
200	.0260	.0196	.0142	.0079	.00252
400	.0271	.0198	.0152	.0122	.00232
800	.0251	.0210	.0165	.00985	.00192
1200	.0288	.0222	.0164	.0098	.00311
1600	.0252	.0220	.0167	.0119	.00325

TABLE 54.—*Comparison of the temperature coefficients of conductivity of lithium nitrate.—Continued.*

$\nu$	In mixtures of acetone and water.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	0.0323	0.0415	0.0394	0.0292	0.00755
10	.0323	.0423	.0415	.0298	.00493
25	.0334	.0427	.0425	.0308	.00532
50	.0334	.0430	.0427	.0316	.00447
100	.0340	.0460	.0442	.0322	.00310
200	.0342	.0450	.0425	.0333	.00252
400	.0341	.048	.0433	.0325	.00232
800	.0340	.043	.0440	.0322	.00192
1200	.0332	.0425	.0425	.0320	.00311
1600	.0330	.0430	.0435	.0331	.00325

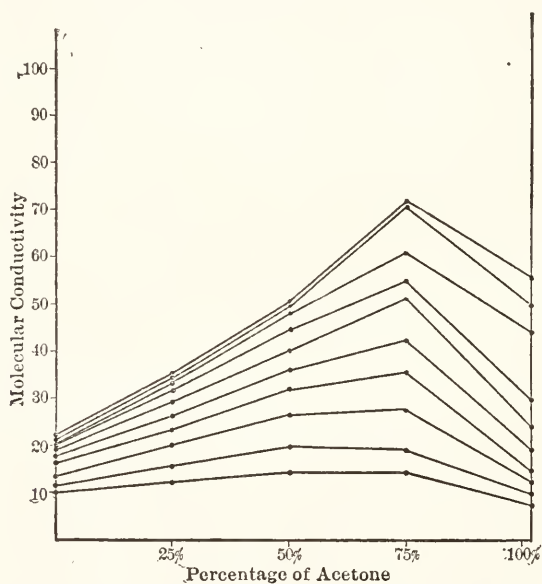


FIG. 24.—CONDUCTIVITY OF LITHIUM NITRATE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 0°.

Table 54 (figs. 24 and 25) shows the same characteristics for lithium nitrate in mixtures of acetone and ethyl alcohol as those observed for the same salt in mixtures of acetone and methyl alcohol, but there is not such a well-defined maximum in these curves.

Table 54 (figs. 26 and 27) for lithium nitrate, in mixtures of acetone and water, shows, at low temperatures and at high dilution, the minimum which is familiar under similar circumstances in mixtures of the alcohols and water. There is, however, even in this case, a tendency towards a maximum, which

results in an inflection-point in most of the curves. It should be especially noticed that the curves diverge from each other rapidly between the 75 per cent mixture and pure acetone. This seems to indicate that the dissociation is greatly increased by the addition of small amounts of water.

POTASSIUM IODIDE.

The salt gave no test for the presence of an iodate, and the flame test showed no appreciable impurity. The salt was dried at 100° to 110° and kept in a desiccator. The salt dissolved in acetone, giving only a very slight coloration.

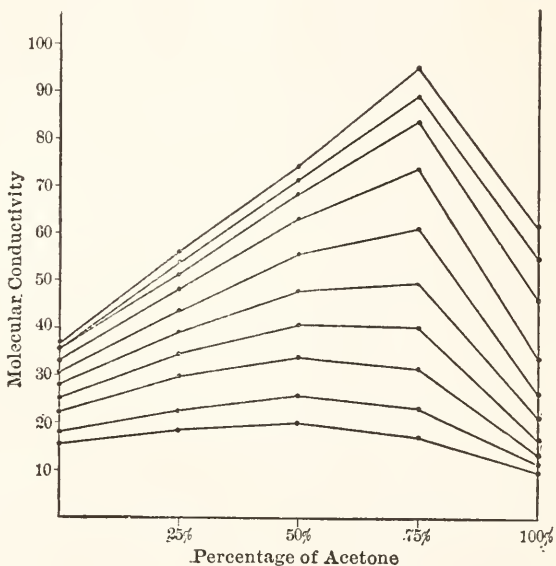


FIG. 25. — CONDUCTIVITY OF LITHIUM NITRATE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 25°.

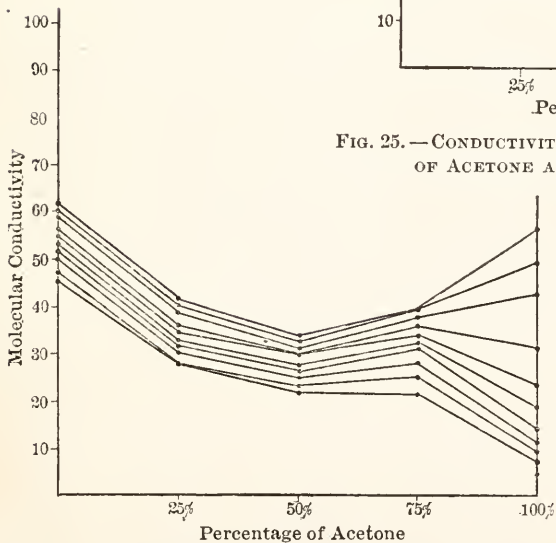


FIG. 26. — CONDUCTIVITY OF LITHIUM NITRATE IN MIXTURES OF ACETONE AND WATER AT 0°.

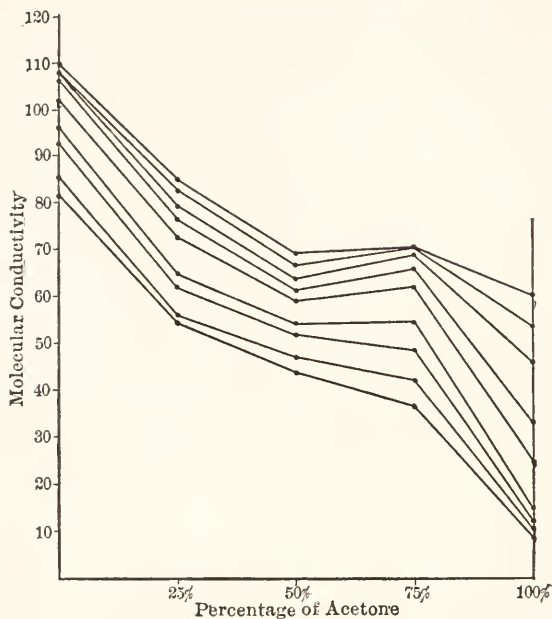


FIG. 27.—CONDUCTIVITY OF LITHIUM NITRATE IN MIXTURES OF ACETONE AND WATER AT 25°.

TABLE 55.—Conductivity of potassium iodide at 0° and 25°.

$\nu$	In methyl alcohol.			In a mixture of 25 p. ct. acetone and methyl alcohol.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
200	65.7	91.4	0.0156	74.1	101.5	0.0148
300	68.1	94.6	.0156	75.6	103.7	.0151
400	68.8	96.3	.0159	77.6	106.1	.0147
600	70.1	99.0	.0165	78.1	108.8	.0157
800	70.6	100.5	.0169	82.3	113.4	.0151
1000	71.1	101.9	.0174	80.8	113.8	.0163
1200	71.4	102.4	.0174	82.8	113.8	.0149
1600	71.7	103.3	.0176	83.9	116.5	.0155

$\nu$	In a mixture of 50 p. ct. acetone and methyl alcohol.			In a mixture of 75 p. ct. acetone and methyl alcohol.			In acetone.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
200	82.7	110.3	0.0133	93.1	117.0	0.0103	100.4	118.0	0.00701
300	85.2	114.7	.0139	95.6	123.0	.0115	105.8	126.2	.00772
400	87.2	114.8	.0127	97.8	124.3	.0108	108.9	128.7	.00730
600	89.6	118.6	.0129	100.4	129.0	.0110	112.3	134.1	.00775
800	91.9	121.8	.0130	104.1	131.8	.0106	116.2	138.6	.00772
1000	93.6	123.1	.0126	103.7	132.7	.0120	118.4	141.6	.00785
1200	93.7	126.2	.0139	104.3	135.7	.0118	118.2	140.3	.00750
1600	94.1	129.2	.0149	106.5	137.7	.0117	120.0	141.1	.00704

TABLE 55.—*Conductivity of potassium iodide at 0° and 25°.*—Continued.

<i>v</i>	In ethyl alcohol.			In a mixture of 25 per cent acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
200	22.0	34.6	0.0230	35.5	52.5	0.0192
300	23.2	36.5	.0241	36.4	54.2	.0196
400	23.8	37.3	.0238	37.8	56.3	.0196
600	25.5	39.1	.0212	38.8	58.0	.0197
800	26.2	39.9	.0209	40.3	60.5	.0200
1000	27.3	41.2	.0202	39.8	59.7	.0200
1200	27.9	41.8	.0200	39.7	60.8	.0212
1600	28.6	42.8	.0194	40.1	63.5	.0232
<i>v</i>	In a mixture of 50 p. ct. acetone and ethyl alcohol.			In a mixture of 75 p. ct. acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
200	52.2	71.4	0.0146	72.0	92.7	0.0115
300	53.4	74.0	.0155	75.3	97.5	.0118
400	56.1	76.8	.0148	78.0	100.1	.0113
600	57.5	79.1	.0150	79.5	102.4	.0115
800	59.5	82.6	.0155	82.4	106.0	.0114
1000	59.7	82.9	.0155	81.8	105.4	.0115
1200	59.8	82.9	.0154	82.7	107.1	.0118
1600	61.3	85.4	.0157	84.8	109.0	.0114
<i>v</i>	In water.			In a mixture of 25 p. ct. acetone and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
200	76.7	136.3	0.0310	44.6	91.1	0.0392
300	77.2	138.3	.0316	44.7	92.7	.0430
400	77.5	138.8	.0318	45.3	92.4	.0416
600	78.0	139.8	.0312	46.1	95.6	.0430
800	78.0	140.1	.0318	47.0	96.9	.0425
1000	78.0	140.6	.0320	46.3	96.2	.0432
1200	78.0	140.7	.0322	47.5	102.9	.0485
1600	78.0	140.7	.0322	47.8	100.1	.0438
<i>v</i>	In a mixture of 50 p. ct. acetone and water.			In a mixture of 75 p. ct. acetone and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
200	36.3	73.8	0.0413	41.6	74.1	0.0311
300	36.8	75.9	.0425	41.9	74.1	.0308
400	37.2	76.3	.0420	42.2	74.6	.0304
600	37.6	77.7	.0427	42.8	75.4	.0302
800	38.6	79.4	.0423	43.7	79.7	.0330
1000	39.0	80.9	.0430	42.2	76.4	.0320
1200	38.4	80.6	.0439	42.8	76.1	.0310
1600	37.5	78.8	.0440	44.1	79.7	.0321

TABLE 56. — Comparison of the conductivities of potassium iodide.

$\nu$	In mixtures of acetone and methyl alcohol.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
200	65.7	74.1	82.7	93.1	100.4	91.4	101.5	110.3	117.0	118.0
300	68.1	75.6	85.2	95.6	105.8	94.6	103.7	114.7	123.0	126.2
400	68.8	77.6	87.2	97.8	108.9	96.3	106.1	114.8	124.3	128.7
600	70.1	78.1	89.6	100.4	112.3	99.0	108.8	118.6	129.0	134.1
800	70.6	82.3	91.9	104.1	116.2	100.5	113.4	121.8	131.8	138.6
1000	71.1	80.8	93.6	103.7	118.4	101.9	113.8	123.1	132.7	141.6
1200	71.4	82.8	93.7	104.3	118.2	102.4	113.8	126.2	135.7	140.3
1600	71.7	83.9	94.1	106.5	120.0	103.3	116.5	129.2	137.7	141.1

$\nu$	In mixtures of acetone and ethyl alcohol.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
200	22.0	35.5	52.2	72.0	100.4	34.6	52.5	71.4	92.7	118.0
300	23.2	36.4	53.4	75.3	105.8	36.5	54.2	74.0	97.5	126.2
400	23.8	37.8	56.1	78.0	108.9	37.3	56.3	76.8	100.1	128.7
600	25.5	38.8	57.5	79.5	112.3	39.1	58.0	79.1	102.4	134.1
800	26.2	40.3	59.5	82.4	116.2	39.9	60.5	82.6	106.0	138.6
1000	27.3	39.8	59.7	81.8	118.4	41.2	59.7	82.9	105.4	141.6
1200	27.9	39.7	59.8	82.7	118.2	41.8	60.8	82.9	107.1	140.3
1600	28.6	40.1	61.3	84.8	120.0	42.8	63.5	85.4	109.0	141.1

$\nu$	In mixtures of acetone and water.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
200	76.7	44.6	36.3	41.6	100.4	136.3	91.1	73.8	74.1	118.0
300	77.2	44.7	36.8	41.9	105.8	138.3	92.7	75.9	74.1	126.2
400	77.5	45.3	37.2	42.2	108.9	138.8	92.4	76.3	74.6	128.7
600	78.0	46.1	37.6	42.8	112.3	139.8	95.6	77.7	75.4	134.1
800	78.0	47.0	38.6	43.7	116.2	140.1	96.9	79.4	79.7	138.6
1000	78.0	46.3	39.0	42.4	118.4	140.6	96.2	80.9	76.4	141.6
1200	78.0	47.5	38.4	42.8	118.2	140.7	102.9	80.6	76.1	140.3
1600	78.0	47.8	37.5	44.1	120.0	140.7	100.1	78.8	79.7	141.1

TABLE 57. — Comparison of the temperature coefficients of conductivity of potassium iodide from 0° to 25°.

$\nu$	In mixtures of acetone and methyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
200	0.0156	0.0148	0.0133	0.0103	0.00701
300	.0156	.0151	.0139	.0115	.00772
400	.0159	.0147	.0127	.0108	.00730
600	.0165	.0157	.0129	.0110	.00775
800	.0169	.0151	.0130	.0106	.00772
1000	.0173	.0163	.0126	.0120	.00785
1200	.0174	.0149	.0159	.0118	.00750
1600	.0176	.0155	.0149	.0117	.00704

TABLE 57. — Comparison of the temperature coefficients of conductivity of potassium iodide from 0° to 25°. — Continued.

$\nu$	In mixtures of acetone and ethyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
200	0.0230	0.0192	0.0146	0.0115	0.00701
300	.0241	.0196	.0155	.0118	.00772
400	.0238	.0196	.0148	.0113	.00730
600	.0212	.0197	.0150	.0115	.00775
800	.0209	.0200	.0155	.0114	.00772
1000	.0202	.0200	.0155	.0115	.00785
1200	.0200	.0212	.0154	.0118	.00750
1600	.0194	.0232	.0157	.0114	.00704

$\nu$	In mixtures of acetone and water.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
200	0.0310	0.0392	0.0413	0.0311	0.00701
300	.0316	.0430	.0425	.0308	.00772
400	.0318	.0416	.0420	.0304	.00730
600	.0312	.0430	.0427	.0302	.00775
800	.0318	.0425	.0423	.0330	.00772
1000	.0320	.0432	.0430	.0320	.00785
1200	.0322	.0485	.0439	.0310	.00750
1600	.0322	.0438	.0440	.0321	.00704

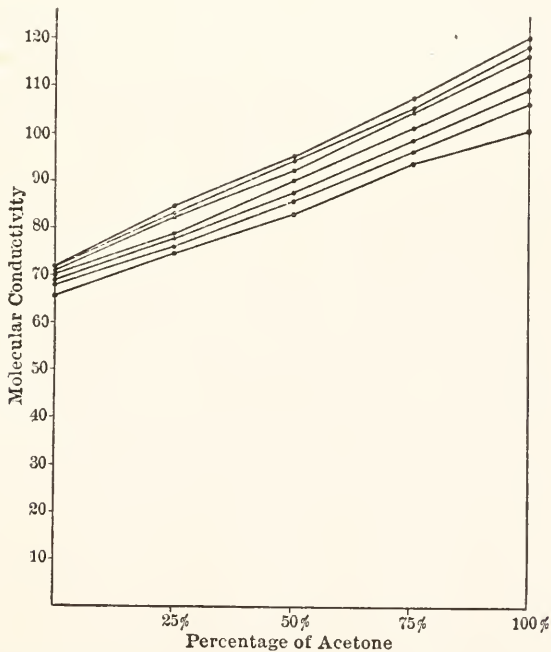


FIG. 28. — CONDUCTIVITY OF POTASSIUM IODIDE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 0°.

Tables 55 and 56 (figs. 28 and 29), for potassium iodide in mixtures of acetone and methyl alcohol, show that the conductivity is almost exactly what we should expect from the law of averages. There is, however, a slight tendency towards a maximum as we raise the temperature. In this respect the results are similar to those obtained with lithium nitrate. The values for the conductivity of potassium iodide in pure water, and ethyl and methyl alcohols, were taken from the work of Jones and Lindsay.

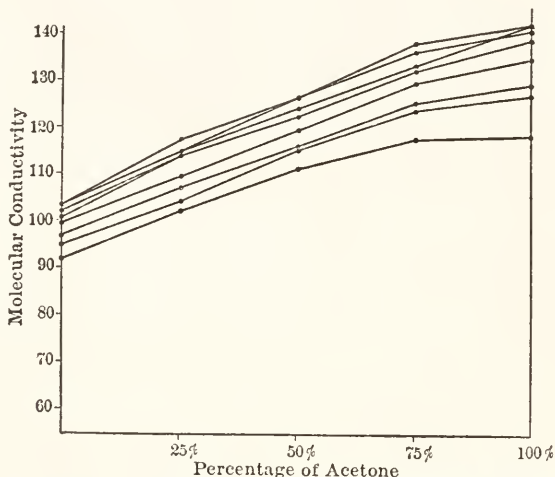


FIG. 29. — CONDUCTIVITY OF POTASSIUM IODIDE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 25°.

Tables 56 and 57 (figs. 30 and 31) show the same characteristics for potassium iodide, in mixtures of acetone and ethyl alcohol, as those observed for the same salt in mixtures of acetone and methyl alcohol, but there is less of a tendency towards a maximum. In fact, there is a slight sagging in the curves. It is observed that this statement is almost identical with the one in regard to lithium nitrate in mixtures of acetone and ethyl alcohol.

Tables 55 and 56 (figs. 32 and 33), for potassium iodide in mixtures of acetone and water, display a minimum in molecular conductivity. There is no tendency towards a maximum. It should, however, be noticed that the divergence of the curves between the 75 per cent mixture and pure acetone is small. The salt is, therefore, quite largely dissociated at all dilutions in all of the mixtures.

It was thought advisable, at this stage, to use solutions of sodium iodide in the various mixtures. Solutions of sodium iodide in acetone had been investigated by Carrara,<sup>1</sup> by Dutoit and Friderich,<sup>2</sup> and by Jones.<sup>3</sup> It was

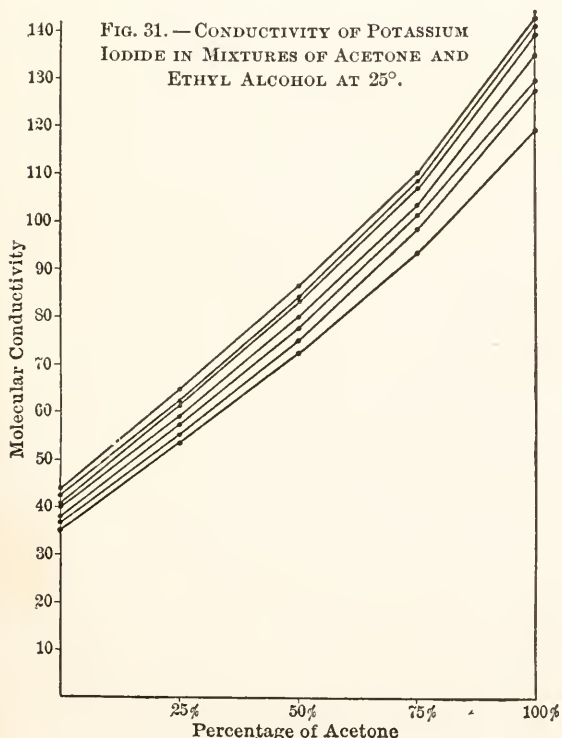
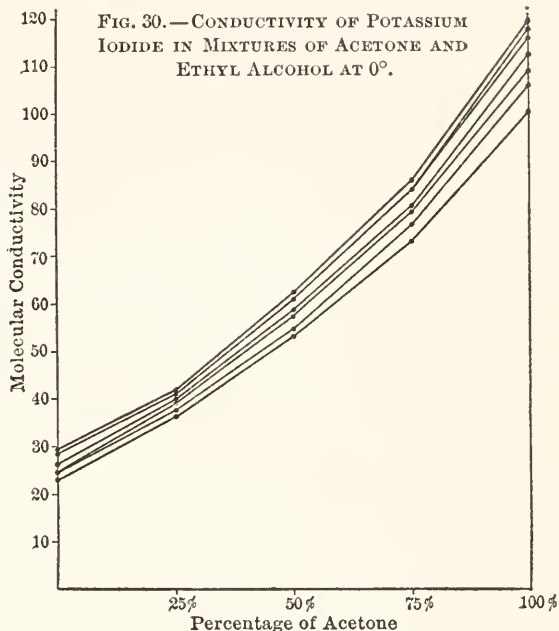
<sup>1</sup> Gazz. Chim. Ital., [1] 27, 207 (1897).

<sup>2</sup> Amer. Chem. Journ., 27, 16 (1902).

<sup>3</sup> Bull. Soc. Chim., [3] 19, 334 (1898).



noticed, however, that the solution had a high coloration, which deepened on standing. Moreover, there was a slight deposit formed at the same time. On evaporation the residue was still colored. The strongest solutions of the sodium iodide, in acetone, gave a test for iodine with starch paste, while the more dilute solutions, though still somewhat colored, gave none. Free iodine was then added to pure acetone until the same color was reproduced. This solution, tested with starch



paste, gave no test for iodine. Time did not permit the further investigation of this interesting point.

CALCIUM NITRATE.

The calcium nitrate used was an anhydrous preparation obtained from Kahlbaum. It was heated for several days at 140°, until it had a constant weight. Subsequently, it was dried for some time at 140° after each exposure to the air. The salt contained no calcium oxide after heating, and showed no appreciable impurity by the flame test.

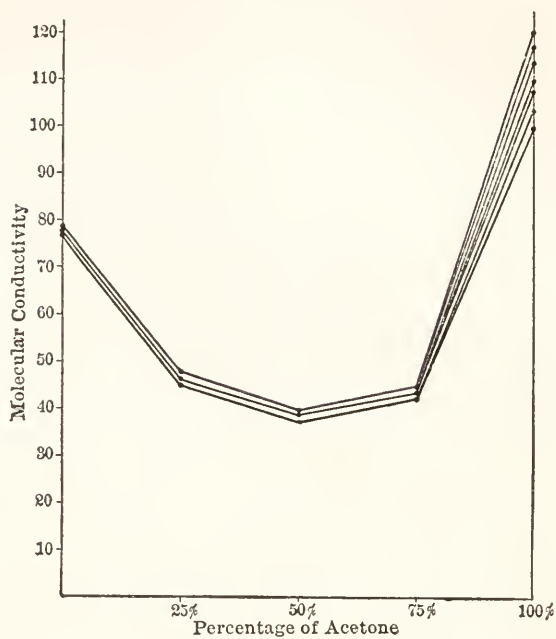


FIG. 32.—CONDUCTIVITY OF POTASSIUM IODIDE IN MIXTURES OF ACETONE AND WATER AT 0°.

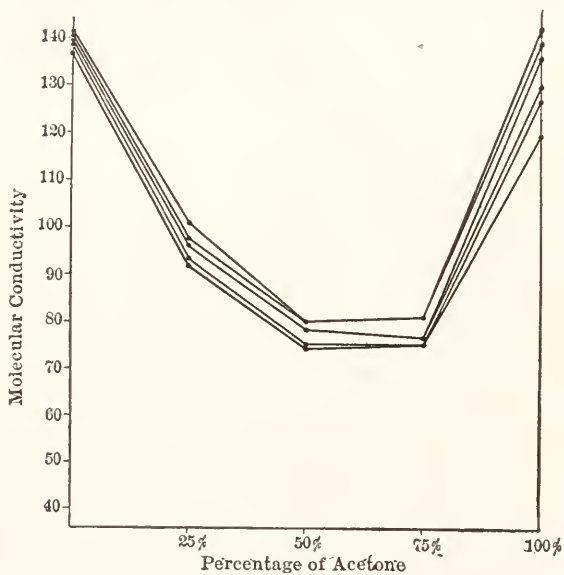


FIG. 33.—CONDUCTIVITY OF POTASSIUM IODIDE IN MIXTURES OF ACETONE AND WATER AT 25°.

TABLE 58. — Conductivity of calcium nitrate at 0° and 25°.

$v$	In methyl alcohol.				
	$\mu_v 0^\circ$	$\mu_v 0^\circ$ (Carroll).	$\mu_v 25^\circ$	$\mu_v 25^\circ$ (Carroll).	Temperature coefficient.
5	14.33	....	19.67	....	0.0149
10	18.98	....	25.38	....	.0135
16	....	....	....	32.79	....
25	27.66	....	36.77	....	.0131
32	....	31.30	....	41.88	.0135
50	34.6	....	45.7	....	.0128
64	....	37.27	....	50.79	.0145
100	42.2	....	55.9	....	.0130
128	....	46.66	....	60.52	.0119
200	49.9	....	65.4	....	.0124
256	....	55.17	....	73.98	.0136
400	58.2	....	75.6	....	.0120
800	65.7	....	86.6	....	.0127
1200	74.4	....	95.0	....	.0111
1600	77.2	....	98.2	....	.0109

$v$	In a mixture of 25 p. ct. acetone and methyl alcohol.			In a mixture of 50 p. ct. acetone and methyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
5	13.13	17.36	0.0129	10.16	12.97	0.0111
10	17.76	23.08	.0120	13.82	17.29	.0100
25	26.33	33.74	.0111	21.30	26.11	.00903
50	33.9	43.2	.0110	28.11	34.44	.00895
100	42.1	53.9	.0112	35.7	42.8	.00795
200	50.7	66.8	.0127	45.2	54.8	.0085
400	60.9	76.8	.0105	55.3	68.3	.0088
800	71.0	89.4	.0104	66.8	83.0	.0097
1200	79.7	98.0	.0092	73.5	91.3	.0097
1600	82.6	102.7	.0098	79.2	98.8	.0099

$v$	In a mixture of 75 p. ct. acetone and methyl alcohol.			In acetone.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
5	6.07	7.65	0.0104	3.93	4.96	0.0105
10	8.10	9.78	.0083	4.44	5.67	.0111
25	12.40	14.56	.0070	5.06	6.55	.0118
50	16.29	19.47	.0078	5.34	6.90	.0117
100	21.65	25.1	.00635	5.48	7.06	.0115
200	28.5	33.0	.00630	5.93	7.54	.0109
400	38.1	44.3	.0065	6.69	8.22	.00916
800	49.2	57.8	.00698	7.93	9.69	.00884
1200	57.3	66.9	.0067	9.26	11.22	.00847
1600	64.2	75.1	.0068	10.36	12.62	.00873

$v$	In ethyl alcohol.			In a mixture of 25 p. ct. acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
5	3.80	5.94	0.022	4.45	6.18	0.0156
10	5.13	7.86	.021	6.01	8.29	.0151
25	7.69	11.67	.020	9.29	12.5	.0140
50	9.80	14.9	.024	12.20	16.59	.0144
100	11.9	18.4	.024	15.4	21.1	.0148
200	14.3	22.4	.024	....	....	....
400	15.2	23.7	.022	22.3	32.2	.0177
800	17.2	27.5	.024	27.2	40.1	.0190
1200	18.1	29.5	.024	28.9	42.7	.0191
1600	18.8	33.3	.031	31.6	46.3	.0186

TABLE 58.—*Conductivity of calcium nitrate at 0° and 25°.*—Continued.

<i>v</i>	In a mixture of 50 p. ct. acetone and ethyl alcohol.			In a mixture of 75 p. ct. acetone and ethyl alcohol.		
	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temperature coefficient.	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temperature coefficient.
5	4.42	5.86	0.0130	3.89	5.08	0.0123
10	6.00	7.64	.0109	4.80	5.99	.00992
25	9.25	11.48	.00963	6.92	8.22	.00753
50	12.33	15.24	.00945	9.20	11.34	.00930
100	16.1	19.9	.00942	12.1	13.8	.0056
200	20.7	26.0	.0102	16.2	18.3	.0052
400	26.1	32.8	.0102	21.3	24.3	.00562
800	31.8	41.4	.0121	28.1	32.7	.0065
1200	35.8	46.8	.0123	33.2	39.1	.0073
1600	38.0	50.7	.0134	36.2	42.4	.0068

<i>v</i>	In water.			In a mixture of 25 p. ct. acetone and water.		
	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temperature coefficient.	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temperature coefficient.
5	80.3	146.8	0.0331	49.9	101.0	0.0410
10	89.8	165.5	.0333	55.0	112.3	.0417
25	98.2	184.2	.0350	60.2	123.9	.0423
50	107.0	192.2	.0313	64.8	134.0	.0427
100	110.4	204.7	.0341	70.3	144.7	.0423
200	114.9	214.2	.0343	72.3	154.1	.0452
400	119.9	222.2	.0341	74.1	154.9	.0441
800	123.4	232.2	.0351	76.8	161.0	.0438
1200	....	238.5	....	79.1	165.4	.0436
1600	128.3	249.8	.0378	80.0	167.7	.0439

<i>v</i>	In a mixture of 50 p. ct. acetone and water.			In a mixture of 75 p. ct. acetone and water.		
	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temperature coefficient.	$\mu_{0^{\circ}}$	$\mu_{25^{\circ}}$	Temperature coefficient.
5	36.9	73.4	0.0392	25.0	43.1	0.0290
10	42.2	84.6	.0402	31.3	52.8	.0272
25	46.7	94.8	.0413	40.1	68.3	.0281
50	50.9	104.7	.0423	45.8	79.2	.0291
100	54.8	115.4	.0449	52.6	92.3	.0300
200	59.6	120.3	.0458	58.4	102.5	.0301
400	61.4	128.0	.0435	62.6	114.9	.0331
800	64.0	133.1	.0433	71.6	126.9	.031
1200	66.1	137.9	.0434	75.1	133.5	.031
1600	66.2	139.8	.0444	76.7	137.7	.032

TABLE 59.—*Comparison of the conductivities of calcium nitrate.*

<i>v</i>	In mixtures of acetone and methyl alcohol.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	14.33	13.13	10.16	6.07	3.93	19.67	17.36	12.97	7.65	4.96
10	18.98	17.76	13.82	8.10	4.44	25.38	23.08	17.29	9.78	5.67
25	27.66	26.33	21.30	12.40	5.06	36.77	33.74	26.11	14.56	6.55
50	34.6	33.9	28.11	16.29	5.34	45.7	43.2	34.44	19.47	6.90
100	42.2	42.1	35.7	21.65	5.48	55.9	53.9	42.8	25.1	7.06
200	49.9	50.7	45.2	28.5	5.93	65.4	66.8	54.8	33.0	7.54
400	58.2	60.9	55.3	38.1	6.69	75.6	76.8	68.3	44.3	8.22
800	65.7	71.0	66.8	49.2	7.93	86.6	89.4	83.0	57.8	9.69
1200	74.4	79.7	73.5	57.3	9.26	95.0	98.0	91.3	66.9	11.22
1600	77.2	82.6	79.2	64.2	10.36	98.2	102.7	98.8	75.1	12.62

TABLE 59.—Comparison of the conductivities of calcium nitrate.—Continued.

v	In mixtures of acetone and ethyl alcohol.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	3.80	4.45	4.42	3.89	3.93	5.94	6.18	5.86	5.08	4.96
10	5.13	6.01	6.00	4.80	4.44	7.86	8.29	7.64	5.99	5.67
25	7.69	9.29	9.25	6.92	5.06	11.67	12.52	11.48	8.22	6.55
50	9.80	12.20	12.33	9.20	5.34	14.91	16.59	15.24	11.34	6.90
100	11.9	15.4	16.1	12.1	5.48	18.4	21.1	19.9	13.8	7.06
200	14.3	19.1	20.7	16.2	5.93	22.4	26.5	26.0	18.3	7.54
400	15.2	22.3	26.1	21.3	6.69	23.7	32.2	32.8	24.3	8.22
800	17.2	27.2	31.8	28.1	7.93	27.5	40.1	41.4	32.7	9.69
1200	18.1	28.9	35.8	33.2	9.26	29.5	42.7	46.8	39.1	11.22
1600	18.81	31.6	38.0	36.2	10.36	33.3	46.3	50.7	42.4	12.62

v	In mixtures of acetone and water.									
	At 0°.					At 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	80.3	49.9	36.9	25.0	3.93	148.6	101.0	73.4	43.1	4.96
10	89.8	55.0	42.2	31.3	4.44	165.5	112.3	84.6	52.8	5.67
25	98.2	60.2	46.7	40.1	5.06	184.2	123.9	94.8	68.3	6.55
50	107.0	64.8	50.9	45.8	5.34	192.2	134.0	104.7	79.2	6.90
100	110.4	70.3	54.8	52.6	5.48	204.7	144.7	115.4	92.3	7.06
200	114.9	72.3	59.6	58.4	5.93	214.2	154.1	120.3	102.5	7.54
400	119.9	74.1	61.4	62.6	6.69	222.2	154.9	128.0	114.9	8.22
800	123.4	76.8	64.0	71.6	7.93	232.2	161.0	133.1	126.9	9.69
1200	....	79.1	66.1	75.1	9.26	238.5	165.4	137.9	133.5	11.2
1600	128.3	80.0	66.2	76.7	10.4	249.8	167.7	139.8	137.7	12.6

TABLE 60.—Comparison of the temperature coefficients of conductivity of calcium nitrate from 0° to 25°.

v	In mixtures of acetone and methyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	0.0149	0.0129	0.0111	0.0104	0.0105
10	.0135	.0120	.0100	.0083	.0111
25	.0131	.0111	.00903	.0070	.0118
50	.0128	.0110	.00895	.0078	.0117
100	.0130	.0112	.00795	.0063	.0115
200	.0124	.0127	.0085	.0065	.0109
400	.0120	.0105	.0088	.0065	.00916
800	.0127	.0104	.0097	.00698	.00884
1200	.0111	.0092	.0097	.0067	.00847
1600	.0109	.0098	.0099	.0068	.00873

v	In mixtures of acetone and ethyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	0.022	0.0156	0.0130	0.0123	0.0105
10	.021	.0151	.0109	.0083	.0111
25	.020	.0140	.00963	.0070	.0118
50	.024	.0144	.00945	.0078	.0117
100	.024	.0148	.00942	.0093	.0115
200	.024	.0155	.0102	.0056	.0109
400	.022	.0177	.0102	.00562	.00916
800	.024	.0190	.0121	.0065	.00884
1200	.024	.0191	.0123	.0073	.00847
1600	.031	.0186	.0134	.0068	.00873

TABLE 60. — Comparison of the temperature coefficients of conductivity of calcium nitrate from 0° to 25°. — Continued.

$\nu$	In mixtures of acetone and water.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	0.0331	0.0410	0.0392	0.0290	0.0105
10	.0333	.0417	.0402	.0272	.0111
25	.0350	.0423	.0413	.0281	.0118
50	.0313	.0427	.0423	.0291	.0117
100	.0341	.0423	.0449	.0300	.0115
200	.0343	.0452	.0458	.0301	.0109
400	.0341	.0441	.0435	.0331	.00916
800	.0351	.0438	.0433	.031	.00884
1200	....	.0436	.0434	.031	.00847
1600	.0378	.0439	.0444	.032	.00873

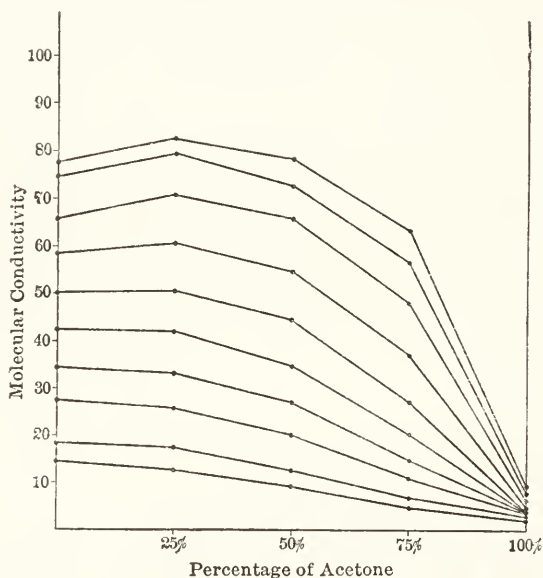


FIG. 34. — CONDUCTIVITY OF CALCIUM NITRATE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 0°.

Tables 58 and 59 (figs. 34 and 35), for calcium nitrate in mixtures of acetone and methyl alcohol, give a pronounced maximum in conductivity at high dilutions. It will be recalled that Jones and Carroll obtained a minimum conductivity with this salt, in mixtures of ethyl alcohol and water, only at low temperatures and at high dilution. It should be noted that calcium nitrate is very slightly dissociated in acetone, and that the maximum occurs in the 25 per cent mixture.

The temperature coefficients of conductivity decrease with the dilution, and they are also less in the mixtures than in the pure solvents, the minimum appearing in the 75 per cent mixture.

Tables 58 and 59 (figs. 36 and 37), for calcium nitrate in mixtures of acetone and ethyl alcohol, show the same characteristics as were observed in the tables for this salt in mixtures of acetone and methyl alcohol; but here the

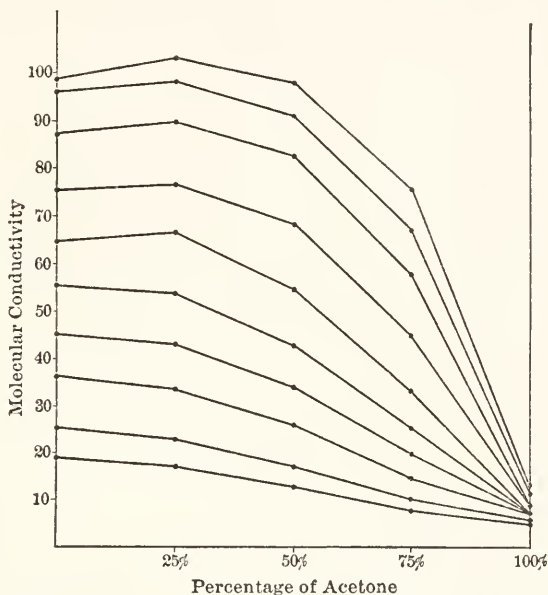


FIG. 35.—CONDUCTIVITY OF CALCIUM NITRATE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 25°.

maximum is more prominent, being present at all dilutions and at both temperatures. The dissociation of calcium nitrate in ethyl alcohol, however, is small. With increasing dilution the maximum shifts from the 25 per cent mixture to the 75 per cent mixture.

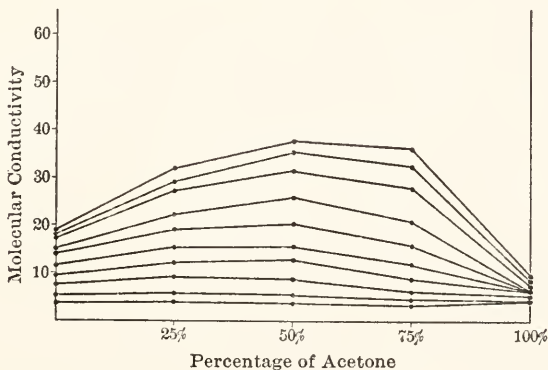


FIG. 36.—CONDUCTIVITY OF CALCIUM NITRATE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 0°.

The temperature coefficients in ethyl alcohol are almost constant, perhaps increasing slightly. The temperature coefficients of the mixtures show a

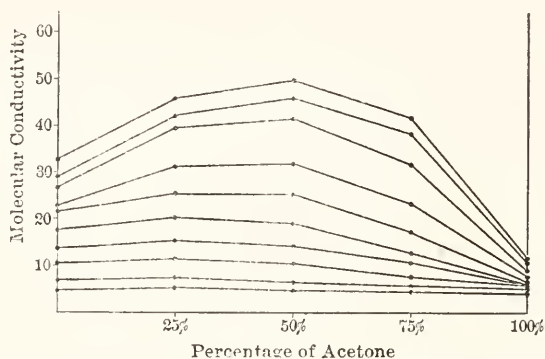


FIG. 37.—CONDUCTIVITY OF CALCIUM NITRATE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 25°.

minimum in the 75 per cent mixture. A similar phenomenon was noticed in the mixtures of acetone and methyl alcohol.

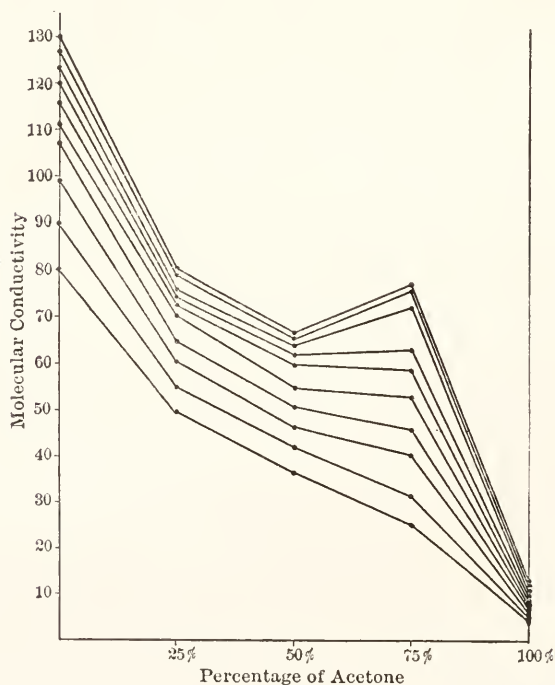


FIG. 38.—CONDUCTIVITY OF CALCIUM NITRATE IN MIXTURES OF ACETONE AND WATER AT 0°.



Tables 58 to 60 (figs. 38 and 39), for calcium nitrate in mixtures of acetone and water, show a point of inflection at low temperatures and high dilution. In concentrated solutions, at high temperatures, the conductivity is what we should expect from the law of averages. These results are similar to those obtained with lithium nitrate in mixtures of acetone and water.

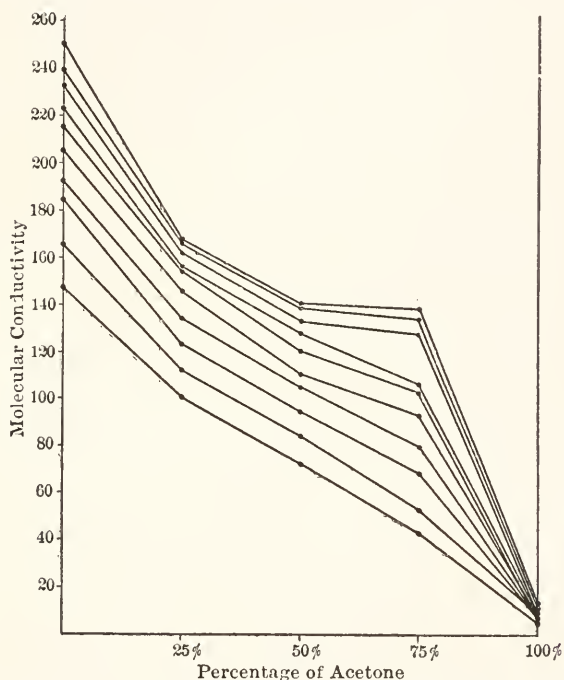


FIG. 39.—CONDUCTIVITY OF CALCIUM NITRATE IN MIXTURES OF ACETONE AND WATER AT 25°.

The temperature coefficients of conductivity of water increase with the dilution, while the temperature coefficients of acetone decrease with the dilution. In the 75 per cent mixture the temperature coefficients are nearly independent of the dilution.

#### VISCOSITY MEASUREMENTS.

In the table of viscosity data (table 61), the values of Thorpe and Rodger<sup>1</sup> for pure water, at 0° and 25°, are taken as the standard, and the other values are referred to them;  $\eta$  represents viscosity,  $\phi$  fluidity, and  $D$  the density of the liquid in question, at 0° and 25°, compared with the density of water at 0° and 25°, respectively.

<sup>1</sup> Phil. Trans., 185A, 307 (1894).

TABLE 61. — *Viscosity measurements.*

At 0° and 25°.	$\nu$	$\eta^0$	$\phi^0$	$\frac{D^0}{\rho^0}$	$\eta^{25^\circ}$	$\phi^{25^\circ}$	$\frac{D^{25^\circ}}{\rho^{25^\circ}}$	Temp. coef.
Water . . . . .	<sup>1</sup> P.S.	0.01778	56.24	1.000	0.00891	112.3	1.000	0.0426
Mixture of 25 p. ct. acetone and water . . . . .	P.S.	.0293	34.12	0.9802	.001276	78.37	0.9710	.0518
Calcium nitrate in mixture of 50 p. ct. acetone and water . . . . .	10 1600 P.S.	.03027	33.03	.9522	.01397 .0133 .0133	71.59 75.13 74.96	.948 .936 .937	.0508
Calcium nitrate in mixture of 75 p. ct. acetone and water . . . . .	10 1600 P.S.	.0170	58.80	.9023	.009617 .009019 .008904	104.0 110.9 112.3	.892 .880 .879	.0364
Calcium nitrate in acetone . . . . .	10 1600 P.S.	.004097	244.1	.8132	.003544 .003255 .003237	282.1 307.3 308.9	.803 .790 .788	.0106
Calcium nitrate in mixture of 25 p. ct. acetone and methyl alcohol . . . . .	10 1600 P.S.	.006498	153.9	.816	.005319 .004604 .004615	188.0 217.2 216.7	.811 .790 .792	.0163
Calcium nitrate in mixture of 50 p. ct. acetone and methyl alcohol . . . . .	10 1600 P.S.	.005336	187.4	.818	.004532 .003926 .003891	220.6 254.7 257.0	.816 .794 .794	.0148
Calcium nitrate in mixture of 75 p. ct. acetone and methyl alcohol . . . . .	10 1600 P.S.	.004501	222.2	.817	.003909 .003480 .003446	255.8 287.3 290.1	.812 .793 .792	.0122
Calcium nitrate in ethyl alcohol . . . . .	5 P.S.	.01856	53.88	.80820	.01373 .01106	72.84 90.35	.81612 .7895	.0271
Calcium nitrate in mixture of 25 p. ct. acetone and ethyl alcohol . . . . .	5 P.S.	.01041	96.08	.81244	.008444 .006714	118.4 148.9	.81822 .791	.0220
Calcium nitrate in mixture of 50 p. ct. acetone and ethyl alcohol . . . . .	5 P.S.	.006801	147.0	.81394	.005861 .004874	170.6 205.2	.81818 .7904	.0148
Calcium nitrate in mixture of 75 p. ct. acetone and ethyl alcohol . . . . .	5 P.S.	.004990	200.4	.81380	.004484 .003776	223.0 264.8	.81709 .7896	.01296

<sup>1</sup> P.S.=pure solvent.TABLE 62. — *Comparison of fluidities.*

Mixtures.	$\nu$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Mixtures of acetone and water at 0° . . . . .	<sup>1</sup> P.S.	56.2	34.12	33.03	58.80	244.1
Calcium nitrate in mixtures of acetone and water at 25° . . . . .	10	....	....	71.59	104.0	282.1
	1600	....	....	75.13	110.9	307.3
Mixture of 50 p. ct. acetone and water at 25° . . . . .	P.S.	112.3	78.37	74.96	112.3	308.9
	....	122.2	153.9	187.4	222.2	244.1
Mixtures of acetone and methyl alcohol at 0° . . . . .	....	122.2	153.9	187.4	222.2	244.1
Calcium nitrate in mixtures of acetone and methyl alcohol at 0° . . . . .	10	161.8	188.0	220.6	255.8	282.1
	1600	180.4	217.2	254.7	287.3	307.3
Mixture of 50 p. ct. acetone and methyl alcohol at 0° . . . . .	P.S.	176.7	216.7	257.0	290.1	308.9
	....	53.88	96.08	147.0	200.4	244.1
Mixture of 75 p. ct. acetone and ethyl alcohol at 0° . . . . .	5	72.84	118.4	170.6	223.0	263.5
	P.S.	90.35	148.9	205.2	264.8	308.9

<sup>1</sup> P.S. = pure solvent.TABLE 63. — *Comparison of the temperature coefficients of fluidity.*

Mixtures.	From 0° to 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Mixtures of acetone and water . . . . .	0.0398	0.0518	0.0508	0.0364	0.0106
Mixtures of acetone and methyl alcohol . . . . .	.0178	.0163	.0148	.0122	.0106
Mixtures of acetone and ethyl alcohol . . . . .	.0271	.0220	.0148	.01296	.0106

Tables 61 to 63 (figs. 40 and 41) show that there is a minimum of fluidity only in the case of acetone and water. In the mixtures of acetone with methyl alcohol we get somewhat larger values than would be expected from the fluidities of the pure solvents. This effect is not so apparent, however, in the case of acetone and ethyl alcohol. These last values were compared with those derived from Dunstan's results, and were found to be almost identical with them.

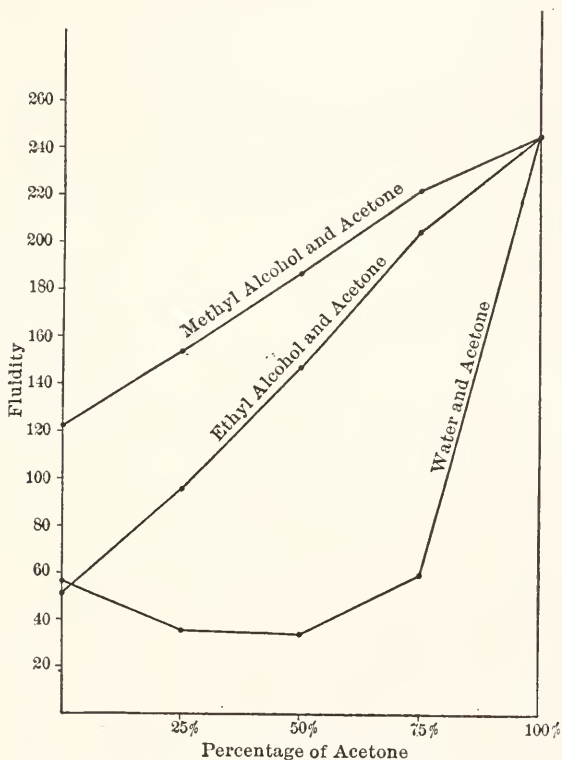


FIG. 40.—FLUIDITY OF SOLVENT MIXTURES AT 0°.

If we compare the viscosity curves of acetone and water, with the fluidity curves, we find that the maximum is more pronounced than the fluidity minimum. The viscosity curves for mixtures of acetone and the alcohols show a marked sagging, as Dunstan has pointed out.

Table 64 shows that although the temperature coefficients of conductivity and fluidity vary in the same manner, the former are uniformly smaller than the latter.

TABLE 64. — Comparison of the temperature coefficients of conductivity and fluidity.

	$v$	Solute.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	Mixture.
Fluidity . .	Pure solv't	.....	0.0398	0.0518	0.0508	0.0364	0.0106	} Acetone and water.
	5	Ca(NO <sub>3</sub> ) <sub>2</sub>	.0331	.0410	.0392	.0290	.01050	
	1600	..	.0378	.0439	.0444	.0320	.00873	
	5	LiNO <sub>3</sub>	.0323	.0415	.0394	.0292	.00755	
Conductivity	1600	..	.0330	.0430	.0435	.0331	.00325	} Acetone and ethyl alcohol.
	200	KI	.0310	.0392	.0413	.0311	.00701	
	1600	..	.0322	.0438	.0440	.0321	.00704	
	Pure solv't	.....	0.0271	0.0220	0.0148	0.01296	0.0106	
5	Ca(NO <sub>3</sub> ) <sub>2</sub>	.022	.0156	.0130	.0123	.0105		
1600	..	.031 (?)	.0186	.0134	.0068	.00873		
5	LiNO <sub>3</sub>	.0241	.0195	.0142	.00795	.00755		
Conductivity	1600	..	.0252	.0220	.0167	.0119	.00325	} Acetone and methyl alcohol.
	200	KI	.0230	.0192	.0146	.0115	.00701	
	1600	..	.0194	.0232	.0157	.0114	.00704	
	Pure solv't	.....	0.0178	0.0163	0.0148	0.0122	0.0106	
5	Ca(NO <sub>3</sub> ) <sub>2</sub>	.0149	.0129	.0111	.104	.0105		
1600	..	.0109	.0098	.0099	.0068	.00873		
5	LiNO <sub>3</sub>	.0152	.0129	.0103	.0104	.00755		
Conductivity	1600	..	.0160	.0146	.0117	.0112	.00325	} Acetone and methyl alcohol.
	200	KI	.0156	.0148	.0133	.0103	.00701	
	1600	..	.0176	.0155	.0149	.0117	.00704	

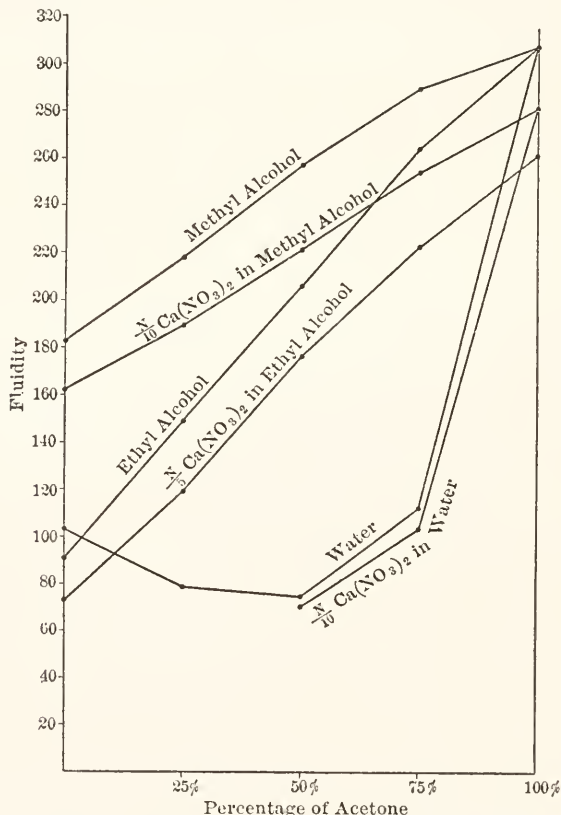


FIG. 41. — FLUIDITY OF SOLVENT MIXTURES AT 25°.

## DISCUSSION OF RESULTS.

The curves for the conductivity of potassium iodide in all of the different mixtures are very similar to the curves of fluidity in the corresponding mixtures. Lithium nitrate and calcium nitrate in all mixtures, at low temperatures, show a deviation from the fluidity curves, particularly in the 75 per cent mixtures, tending to produce a maximum in conductivity.

The work of Jones and Lindsay and of Jones and Carroll showed that solutions of lithium nitrate, in mixtures of methyl alcohol and water, gave curves with a simple minimum, like the fluidity curves for the corresponding mixtures. Calcium nitrate, dissolved in the same mixtures, and also in mixtures of ethyl alcohol and water, in no case gave a minimum according to Jones and Carroll; consequently their curves are not similar to the corresponding fluidity curves.

Our results differ fundamentally from those heretofore observed, in that the mixtures of acetone with the alcohols and water show a tendency towards a maximum in the conductivity of solutions of certain salts, such as lithium nitrate and calcium nitrate.

Since conductivity is dependent upon fluidity, and not *vice versa*, we shall discuss first the fluidity curves, and then the conductivity curves in connection with them.

When methyl alcohol or ethyl alcohol is mixed with acetone, the fluidity curve of the mixtures is a straight line. This is what we should expect, if the fluidity of each of the components has its proportionate effect. Hence we may conclude that the molecular aggregations of these pure solvents are not essentially changed in regard to size by mixing the two solvents. We have already shown that the work of Thorpe and Rodger, Traube, Varenne and Godefroy, and others has made it evident that viscosity is dependent upon the character of the molecular aggregations present.

It may be objected that a straight line is not the "normal" fluidity curve, since, heretofore, a straight line has been considered to be the normal viscosity curve, and the two conceptions are, in general, incompatible. To make this clear, let us suppose that we mix two liquids which are made up of particles which have no unusual action on each other, *i. e.*, do not form new aggregations of any kind. Two monomolecular liquids which do not form complexes on mixing would fulfill this condition. Further, let us suppose that the liquid is allowed to flow through a tube. The resulting fluidity would be the sum of the partial fluidities of the components. That is, the more rapidly moving particles would be held back by the slower ones, and the motion would be a mean value, proportional to the relative amounts of the components. Formulated, this would be

$$(m_1 + m_2)\phi = m_1\phi_1 + m_2\phi_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $m_1$  and  $m_2$  are the amounts of the components, and  $\phi_1$  and  $\phi_2$  are their respective fluidities.

This is similar to the conception which we have in electricity, where the conductance of two or more conductors is represented by the sum of their separate conductances. The conductance of a single conductor is expressed by the value  $\frac{c\sigma}{l}$ , where  $c$  is the specific conductivity,  $\sigma$  the cross-section of the conductor, and  $l$  the length. The conductance of a pair of conductors of different material, in parallel, is, per unit length,

$$(\sigma_1 + \sigma_2)c = c_1\sigma_1 + c_2\sigma_2$$

Admitting this reasoning, it becomes evident that conductivity and fluidity are strictly comparable. It will be noticed, moreover, that the *viscosities are not additive*.

If  $\eta_1$  and  $\eta_2$  represent the viscosities of the two components, then, since viscosity is the reciprocal of fluidity, we have from (1) :

$$(m_1 + m_2) \frac{1}{H} = \frac{m_1}{\eta_1} + \frac{m_2}{\eta_2}$$

By making  $m_1$  and  $m_2$  the percentages of the respective components:

$$\begin{aligned} \frac{1}{H} &= \frac{m_1}{\eta_1} + \frac{1 - m_1}{\eta_2} \\ \eta_1\eta_2 &= [m_1\eta_2 + (1 - m_1)\eta_1] H \\ &= [m_1(\eta_2 - \eta_1) + \eta_1] H \dots \dots \dots (2) \end{aligned}$$

Now let

$$m_1(\eta_2 - \eta_1) + \eta_1 = m'_1(\eta_2 - \eta_1)$$

then

$$m'_1 = m_1 + \frac{\eta_1}{\eta_2 - \eta_1}$$

Substituting this value in (2),

$$m'_1 = H \frac{\eta_1\eta_2}{\eta_2 - \eta_1} = \text{constant}$$

which is the equation of the equilateral hyperbola, the Y-axis of which is the distance  $\frac{\eta_1}{\eta_2 - \eta_1}$  to the left of the origin, to which equation (1) is referred.

Thus, we seem justified in concluding that *the hyperbola is the normal curve for viscosities*.

From the above considerations we are led to the belief that inferences drawn from viscosity curves alone may lead to erroneous conclusions. For example, Wijkander<sup>1</sup> reached the conclusion that in no case is the viscosity identical with that calculated by the admixture rule. In the case of mixtures of ether with chloroform, and of ether with carbon disulphide, there were

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<sup>1</sup> Beibl. Wied. Ann., 8, 3 (1879).

inflection-points in the curves, but no simple relation between the viscosity coefficients of a mixture and those of its constituents could be deduced.

Linebarger<sup>1</sup> found that the observed viscosities, in general, were less than those that were calculated by the mixture rule, except, perhaps, in the case of mixtures of benzene and chloroform, and mixtures of carbon disulphide and benzene, toluene, ether, and acetic ether, where, according to Dunstan, the temperature of observation, 25°, was possibly too near the boiling-point of the carbon disulphide to make any specific influence which that liquid might exert at lower temperatures perceptible.

Dunstan<sup>2</sup> makes the significant statement that "the law of mixtures is never accurately obeyed, and divergences seem to be more clearly marked in the case of viscosity than with other properties, such as refractive index."

These discrepancies are explained if our view be accepted, since the divergence in every abnormal case thus far investigated is smaller for the fluidity curves than for the corresponding viscosity curves, and the mixtures with carbon disulphide, which give "normal" viscosity curves, also give *fluidity* curves that are equally satisfactory. In the particular case of acetone and methyl alcohol or ethyl alcohol, the fluidity is a straight line, nearly to within the limits of experimental error, so that these two pairs of liquids may be considered as perfectly normal.

It must be stated explicitly that many of the conclusions arrived at by the above-mentioned workers are not changed by this new method of comparing results, especially since, in many cases, they obtained curves with actual maxima and minima. These effects are reproduced in the fluidities as minima and maxima, respectively, which are generally less prominent than before.

When most of the organic solvents worked with up to this time are mixed with water, there is a very large increase in viscosity. In general, there is also a contraction on mixing these solvents and water. Some of those that give a pronounced maximum of viscosity are methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, acetic acid, propionic acid, butyric acid, isobutyric acid, and acetone. The workers in this field have attributed the increase in viscosity to increase in the size of the molecular aggregations.

This decrease in fluidity retards the movement of the ions, hence there is a fall in molecular conductivity, which explains the minimum in conductivity heretofore observed by Zelinsky and Krapiw, Cohen, Jones and Lindsay, Jones and Carroll, and ourselves. This relation between viscosity and conductivity, as has been shown, has long been recognized. Wiedemann, Stephan, Dutoit and Friderich, and Jones and Carroll have been connected with the development of the exact relation between them.

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<sup>1</sup> Amer. Journ. Sci. [4] 2, 331 (1896).

<sup>2</sup> Journ. Chem. Soc., 85, 817 (1904.) Ztschr. phys. Chem., 49, 590 (1904).

If the salt happens to be highly dissociated in water and very little dissociated in the other solvent, the curves may be at such an angle with the axis of  $X$  that there will be only a sagging of the curve and not an actual minimum. Therefore, the *amount of deviation from the normal curve* appears to us to be a matter of prime importance, while the finding of a *minimum* is not.

If we could make a correction at the different parts of the curve for the different degrees of dissociation in the pure solvents and in the mixtures, we should then have a curve exactly parallel to the fluidity curve, if it is true that fluidity and dissociation are the only factors concerned, as Dutoit and Friderich, and Jones and Carroll supposed. In our case it is almost impossible to make the correction with the data at hand, except, possibly, in the case of potassium iodide. The conductivity values for potassium iodide show that it is nearly dissociated in all mixtures, but with the other salts complete dissociation is not even approximately reached. Thinking that it might be possible to calculate  $\mu_{\infty}$ , we have tested Kohlrausch's formula,

$$\frac{\mu_{\infty} - \mu_v}{C^{\frac{1}{3}}} = K$$

where  $C$  is the concentration and  $K$  is a constant. We found that it did not apply except in aqueous solutions. Völlmer<sup>1</sup> has already shown that the Ostwald dilution law does not apply to solutions in ethyl alcohol and methyl alcohol. Solutions of potassium iodide, in mixtures of methyl alcohol and water, were investigated by Zelinsky and Krapiwins and Jones and Lindsay. The conductivity curves resemble the fluidity curves for methyl alcohol and water, as shown by Jones and Carroll. We have found the same similarity in the case of potassium iodide and water.

If we accept the Kohlrausch and Jones's hypotheses of ionic spheres, it is evident that the atmosphere about the ions remains of the same size throughout all the mixtures; otherwise the ions would tend to show a maximum in conductivity in those mixtures where the atmosphere is smallest, causing a divergence from the fluidity curves. Difference in dissociation would also cause a divergence between the conductivity and fluidity curves. In the above case, however, the dissociation is large and all the curves are parallel.

If we pass now to potassium iodide in mixtures of acetone with methyl alcohol and ethyl alcohol, we find, again, that the conductivity curves and fluidity curves are very similar, *i. e.*, nearly straight lines, with a tendency towards a maximum, which is greater in the case of methyl alcohol than in that of ethyl alcohol. Evidently the changes in the size of the ionic spheres and the changes in the dissociation have either counteracted each other or remained zero.

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<sup>1</sup> Ann. der Phys., 52, 328 (1894).



Now let us consider lithium nitrate. In mixtures of acetone with the alcohols, we get a pronounced maximum in conductivity in the 75 per cent mixtures, at high dilutions. Since these solvents gave no such maximum in the case of potassium iodide, the maximum must be connected with the lithium nitrate itself. There are two possible explanations of the phenomenon: (1) Increase in dissociation in the 75 per cent mixture; (2) increase in the mobility of the ions, due to the diminution in the size of the ionic spheres. We shall attempt to decide between these two possibilities.

We have shown by consideration of the fluidities that the liquids are not more associated in the mixtures than in the pure solvents; hence, if we accept the hypothesis of Dutoit and Aston, that dissociating power increases with the association of the solvent, the maximum can not be due to increase in dissociation in the mixture. For example, calcium nitrate shows a pronounced maximum in conductivity in mixtures of alcohol and acetone, even though the dissociation of calcium nitrate in pure acetone is very small. It hardly seems probable that the acetone increases the dissociation of pure alcohol if it does not form complexes with it. We also have the fact, found by Jones and Carroll, that even in the case of alcohol and water, where molecular aggregations are known to be formed, there is not an increase in dissociation larger than the possible experimental error. Furthermore, if the 75 per cent mixture has the highest dissociating power, we should not expect to find the maximum moving from the 25 per cent mixture to beyond the 75 per cent mixture, as the concentration of the dissolved substance decreases. This is the case with lithium nitrate, in mixtures of the alcohols and acetone. Finally, the maximum in conductivity should manifest itself in the most concentrated solutions of potassium iodide, in mixtures of acetone with the alcohols. This is contrary to the facts. We, therefore, accept, tentatively, the view that *the maximum in conductivity is due, primarily, to a change in the dimensions of the ionic spheres.*

The determination, however, of the dissociation of lithium nitrate in pure alcohol, in pure acetone, and in a 75 per cent mixture of these solvents, would be a very important check. Through the kindness of Mr. L. McMaster this point has been tested for acetone and ethyl alcohol, as shown in table 65.

TABLE 65. — *Conductivity of lithium nitrate ( $\mu_v$  25° corrected).*

$v$	In pure acetone at 25°.	In mixture of 75 p. ct. acetone and ethyl alcohol at 25°.	In pure alcohol at 25°.
2000	55.28	92.66	37.01
2500	62.87	100.55	41.04
3000	66.42	101.88	41.48

The conductivity of the pure acetone used in these experiments was  $1.516 \times 10^{-6}$ ; that of the pure alcohol,  $0.857 \times 10^{-6}$ .

These results show that complete dissociation is nearly reached only in the pure alcohol, and that the mixture is dissociated about as we might expect from the law of averages. We note that the maximum is very pronounced.

The conclusion of Dutoit and Friderich and of Jones and Carroll, that conductivity is inversely proportional to viscosity, and directly proportional to the association factor of the solvent (or to the amount of dissociation), is incomplete. It fails to take into consideration changes in the dimensions of the ionic spheres.

In the conductivities of lithium nitrate, in mixtures of acetone and water, the decreased fluidity manifests itself again. We notice, however, that the power of the acetone to produce smaller (or more symmetrical) ionic spheres is not destroyed by substituting water for methyl alcohol or ethyl alcohol. Practically all of the dilutions in the 75 per cent mixture of acetone and water, show a decided elevation of the conductivity curves above those we should expect from similar measurements with potassium iodide. That increase in dissociation would make itself manifest in this way is doubtful, and our theory is thus strengthened.

Jones and Lindsay's results with lithium nitrate, in mixtures of water and methyl alcohol, do not show this effect; hence the acetone acts peculiarly in this respect. However, acetone behaves exceptionally in other ways.

At this point we should call attention to the fact that lithium forms a very slowly moving ion, *i. e.*, one with a large ionic sphere, while potassium forms a comparatively rapidly moving ion, *i. e.*, one with a small ionic sphere. The anions used do not differ greatly. Calcium forms an ion with a migration velocity between that of lithium and potassium. It was thought best to measure the conductivities of calcium nitrate in all of the mixtures, exactly as with the other salts.

The results show that the tendency towards a maximum in conductivity in the mixtures is very marked indeed. Moreover, they show that calcium nitrate is dissociated in the solvents very differently from lithium nitrate. Calcium nitrate is dissociated to a large extent in water and methyl alcohol, very much less in ethyl alcohol, and still less in acetone. In spite of all differences, we are struck by the fact that the maximum *divergence* still tends to manifest itself in the 75 per cent mixture. Especially is this the case with acetone and water.

Let us now turn our attention to the concentrated solutions. In these we find the tendency towards a maximum very small, or entirely absent. If our explanation is correct, then, as the concentration of the salt increases there will be less of the solvent for the formation of ionic spheres, or, in the

case of mixtures which tend to reduce the large atmospheres of the dilute solutions, the mass action of the solvent is much diminished.

Calcium nitrate is intermediate in its behavior between potassium iodide and lithium nitrate. It seems reasonable to connect this with the migration velocity. It would be interesting to experiment with sodium, the ion of which has a slow migration velocity; but, as we have shown, sodium iodide, although soluble, is unsuited for this purpose.

## SUMMARY.

We have measured the fluidities of mixtures of acetone with methyl alcohol, ethyl alcohol, and water, and of a few solutions of calcium nitrate in these mixtures.

We have measured the conductivity of various concentrations of lithium nitrate, potassium iodide, and calcium nitrate, dissolved in the above mixtures.

These conductivities, in the case of mixtures of acetone and water, exhibit the minimum in conductivity previously observed by several other workers. Moreover, this minimum in conductivity has been shown to be intimately connected with the minimum in fluidity observed in these mixtures, but the conductivity curves of different salts show marked differences.

In the mixtures of acetone and the alcohols, the fluidities are what we should expect from the law of averages, *i. e.*, the fluidity curve is nearly a straight line. From this fact we have concluded that acetone and the alcohols thus far studied do not form more complex molecular aggregations when mixed than were originally present before mixing.

The conductivities of potassium iodide, in mixtures of acetone with methyl alcohol or ethyl alcohol, are also what we should expect from the law of averages — the conductivity curves are nearly straight lines at all dilutions. Again, the conductivity has been shown to be intimately connected with fluidity.

Lithium nitrate and calcium nitrate, however, give a very pronounced *maximum in conductivity*, in mixtures of acetone with methyl alcohol or ethyl alcohol. Evidently this was an unexpected phenomenon; to explain it, all of the factors that could reasonably influence conductivity were collected. After the elimination of several of them, the possible explanations were shown to be, either an increase in dissociation giving rise to more ions, or a diminution in the size of the ionic spheres already in the solution.

It was then shown to be possible to eliminate one of these factors by the following considerations:

(1) The fluidity of the mixtures of acetone and alcohol shows that there is no increase in molecular aggregation, hence we should not expect increased dissociation, if we accept the hypothesis of Dutoit and Aston.

(2) Jones and Carroll have proved that, even in the case of alcohol and water, there is practically no increase in dissociation in the mixtures.

(3) Furthermore, the maximum migrates from the 25 per cent mixture, at high concentration, to the 75 per cent mixture in the more dilute solutions. This would hardly be expected if the dissociating power is greatest in a certain mixture.

(4) Potassium iodide shows no tendency towards a maximum of conductivity in the most concentrated solution with which we worked.

(5) Very recent measurements, at extreme dilution, have failed to show any great difference in the dissociating power of the mixtures from that of the pure solvents.

We, therefore, seemed justified in the conclusion that the maximum in conductivity is due to a change in the dimensions of the atmospheres about the ions.

The conclusion of Dutoit and Friderich and of Jones and Carroll, that conductivity is proportional to the dissociation, and inversely proportional to the viscosity, has been shown to be incomplete in not taking into consideration possible changes in the size of the ionic spheres.

The conductivities of lithium nitrate and calcium nitrate, in mixtures of acetone and water, again show a tendency towards a maximum, in spite of the great diminution in fluidity.

Finally, it has been pointed out that the tendency to form a maximum in conductivity increases from potassium iodide, through calcium nitrate, to lithium nitrate, which seems to show these effects most strongly. This may be connected with the migration velocities of these ions.

## WORK OF ROUILLER.

### OBJECT OF THIS INVESTIGATION.

This work is a direct continuation of the investigation carried out in Johns Hopkins University two years earlier by Jones and Bassett.<sup>1</sup> They wished, if possible, to trace a connection between the phenomena of minimum conductivity, first observed by Zelinsky and Krapiwins<sup>2</sup> and later extensively studied by Jones and Lindsay,<sup>3</sup> which solutions in certain mixtures of alcohol and water exhibit. Jones<sup>4</sup> and his students have extended the investigation of this problem to mixtures of other solvents, including acetone, and have obtained interesting results. It was, therefore, thought desirable to extend also the work of Jones and Bassett. The conductivity of silver nitrate and the transport number of its anion in binary mixtures of water, methyl alcohol, ethyl alcohol, and acetone have been determined at two temperatures, 0° and 25°.

### SOLVENTS.

#### WATER.

The water used in preparing the solutions was purified essentially by the method of Jones and Mackay.<sup>5</sup> Ordinary distilled water was twice redistilled from an acidified solution of potassium dichromate, and the stream from the second distillation passed through a boiling solution of barium hydroxide. It had, at 0°, a conductivity of about  $1.0 \times 10^{-6}$ .

#### METHYL ALCOHOL.

The purest obtainable product was boiled 1 to 2 days with lime, distilled, and allowed to stand over anhydrous copper sulphate till needed. All distillations were made through a Singer fractionating head and a block-tin condenser, and the liquid was protected during distillation from the moisture in the air by means of a soda lime U-tube. To prevent any possibility of soda-lime dust being drawn back into the liquid, the end of the tube nearest to the bottle was covered with filter paper. The first and last portions of the distillate were always discarded. The mean conductivity at 0° =  $0.8 \times 10^{-6}$ .

<sup>1</sup> Amer. Chem. Journ., **32**, 409 (1904).

<sup>2</sup> Ztschr. phys. Chem., **21**, 35 (1896).

<sup>3</sup> Amer. Chem. Journ., **28**, 329 (1902).

<sup>4</sup> Ibid., **32**, 521 (1904); **34**, 481 (1905).

<sup>5</sup> Ibid., **19**, 83.

## ETHYL ALCOHOL.

The best commercial article was treated in the same manner as the methyl alcohol. Its conductivity at  $0^{\circ}$  was about  $0.0 \times 10^{-7}$ .

## ACETONE.

The acetone was allowed to stand over fused calcium chloride before using. Conductivity at  $0^{\circ} = 1.0 \times 10^{-6}$ .

## MIXED SOLVENTS.

The mixture obtained by adding  $n$  c. c. of solvent *A* to  $100 - n$  c. c. of solvent *B*, was designated as an " $n$  per cent *A* -  $(100 - n)$  per cent *B* mixture." This method of preparing mixed solvents was deemed preferable to the more common method of diluting  $n$  c. c. of solvent *A* to 100 c. c. with solvent *B*. In the latter case it is always necessary to state which solvent is used as diluent, and the mixture must always be allowed to cool down to the temperature of the unmixed solvents before the final dilution to the mark on the measuring-flask can be effected.

## CONDUCTIVITY.

## APPARATUS.

In making conductivity measurements, the usual Kohlrausch method, with Wheatstone bridge, induction coil, and telephone receiver, was used. The bridge-wire was of "manganin." The resistance coils were calibrated to within 0.04 per cent.

The conductivity cells were of the type devised by Jones and Bingham<sup>1</sup> for use with volatile solvents, which, like acetone, attack rubber and wax. They differ from the simple Arrhenius cells in that the cup is closed by a ground-glass stopper, into which are sealed with glass the tubes that carry the electrodes.

The electrodes were carefully cleansed with chromic acid and covered with platinum black, by electrolyzing a dilute solution of platinic chloride. All absorbed chlorine was removed with sodium hydroxide, and the plates were washed with dilute hydrochloric acid and distilled water, dried, and heated to redness in the flame of a blast-lamp. Electrodes thus treated gave a good tone minimum, did not appreciably absorb salts from their solutions, and showed no tendency to cause the rapid oxidation of alcohol to acetic acid. When not in use the cells were filled with distilled water. Solutions were never allowed to stand in them longer than was necessary.

The zero-bath was of the form commonly used in this laboratory. A tin pail was filled with finely crushed ice and water, and the cells were then packed into the ice as tightly as possible. The pail was placed in a larger, indurated

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<sup>1</sup> Amer. Chem. Journ., **34**, 481 (1905).

filter bucket, and the intervening space filled with finely crushed ice and water. Such a bath will maintain a temperature of  $0^{\circ}$  to within  $0.1^{\circ}$  for hours. The  $25^{\circ}$  bath was a galvanized-iron tub, lined on the outside with asbestos. The water in it was kept at a uniform temperature by means of a stirrer driven by a small hot-air motor, and could easily be kept to within  $0.1^{\circ}$  of any desired temperature. The thermometers were graduated to  $0.1^{\circ}$  and standardized. The burettes and measuring-flasks were all carefully calibrated by the method of Morse and Blalock.<sup>1</sup>

#### PREPARATION OF SOLUTIONS.

The silver nitrate used in this work was obtained from Kahlbaum, and was perfectly neutral. It was finely pulverized, dried for several hours at  $100^{\circ}$  to  $105^{\circ}$ , and kept in a desiccator in the dark. Somewhat more of the salt than was necessary to prepare a N/50 solution was weighed into the solvent, and the exact concentration was determined by titration with a N/25 solution of ammonium sulphocyanate, with ferric ammonium sulphate as indicator.

The sulphocyanate solution was standardized against a N/25 solution of silver nitrate and weighed quantities of thoroughly dried potassium chloride, which had been especially purified in the physical chemical laboratory of the Johns Hopkins University for use in conductivity work. The solution whose conductivity was to be measured was then made exactly N/50 by the addition of the proper amount of solvent. From this mother-solution the other solutions were prepared by successive dilution. The N/800 and N/1200 solutions were prepared from the N/400.

#### CONDUCTIVITY MEASUREMENTS.

In measuring the conductivity of a solution, readings were always made with three different resistances, and the values given are the mean. Before using, the cells and electrodes were carefully dried and rinsed out with the solution whose conductivity was to be measured. The cell constants were determined with 0.02 N and 0.004 N solutions of pure potassium chloride. The molecular conductivity of the former was taken as 129.7 at  $25^{\circ}$ .

In tables 66 and 67, under  $v$  is given the concentration, expressed in number of liters of the solution containing a gram-molecular weight of the salt; under  $\mu_0$ , the molecular conductivity at  $0^{\circ}$ ; and under  $\mu_{25}$ , the molecular conductivity at  $25^{\circ}$ .

The temperature coefficients are obtained by dividing the increase in conductivity per degree, by the conductivity at  $0^{\circ}$ .

The values for the molecular conductivities in water and methyl and ethyl alcohols are obtained, by interpolation, from the measurements of Jones and Bassett, and the temperature coefficients are calculated from these interpolated values.

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<sup>1</sup> Amer. Chem. Journ., **16**, 479 (1894).

TABLE 66. — *Molecular conductivity of silver nitrate.*

<i>v</i>	In a 75 p. ct. water, 25 p. ct. acetone mixture.		In a 50 p. ct. water, 50 p. ct. acetone mixture.		In a 25 p. ct. water, 75 p. ct. acetone mixture.		In acetone.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
50	38.97	78.79	31.31	62.97	30.79	53.04	....	....
100	40.91	81.82	31.72	64.34	34.59	60.05	....	....
125	....	....	....	....	....	....	7.93	10.08
200	42.36	85.70	33.00	67.69	36.49	63.81	8.18	10.36
400	41.65	85.00	33.74	68.50	38.75	68.34	8.58	11.57
800	43.24	88.24	34.32	71.12	40.35	70.63	9.64	12.08
1200	45.01	91.71	34.57	70.60	40.26	71.28	10.54	13.11
	Conductivity of solvent at $0^\circ = 1.15 \times 10^{-6}$ .		Conductivity of solvent at $0^\circ = 1.66 \times 10^{-6}$ .		Conductivity of solvent at $0^\circ = 2.06 \times 10^{-6}$ .		Conductivity of solvent at $0^\circ = 1.0 \times 10^{-6}$ .	

<i>v</i>	In water and acetone, and mixtures of these solvents.									
	Percentage of acetone at $0^\circ$ .					Percentage of acetone at $25^\circ$ .				
	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
50	63.11	38.97	31.31	30.79	....	111.62	78.79	62.97	53.04	....
100	63.71	40.91	31.72	34.59	....	116.82	81.82	64.34	60.05	....
200	66.51	42.36	33.00	36.49	8.18	121.16	85.70	67.69	63.81	10.36
400	70.19	41.65	33.74	38.75	8.58	125.27	85.00	68.50	68.34	11.57
800	70.94	43.24	34.32	40.35	9.64	125.73	88.24	71.12	70.63	12.08
1200	70.65	45.01	34.57	40.26	10.54	125.43	91.71	70.60	71.28	13.11

<i>v</i>	In a 75 p. ct. methyl alcohol, 25 p. ct. ethyl alcohol mixture.		In a 50 p. ct. methyl alcohol, 50 p. ct. ethyl alcohol mixture.		In a 25 p. ct. methyl alcohol, 75 p. ct. ethyl alcohol mixture.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
50	32.39	45.69	24.06	35.24	17.45	26.54
100	38.01	54.09	29.04	42.39	20.78	31.89
200	44.94	64.40	32.17	47.29	23.40	36.41
400	47.09	67.72	35.93	53.04	26.45	41.32
800	50.45	72.85	39.22	58.10	28.38	44.71
1200	51.66	74.88	40.06	59.68	28.91	46.03
	Conductivity of solvent at $0^\circ = 7.4 \times 10^{-7}$ .		Conductivity of solvent at $0^\circ = 3.1 \times 10^{-7}$ .		Conductivity of solvent at $0^\circ = 3.8 \times 10^{-7}$ .	

<i>v</i>	In methyl and ethyl alcohols, and mixtures of these solvents.									
	Percentage of ethyl alcohol at $0^\circ$ .					Percentage of ethyl alcohol at $25^\circ$ .				
	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. (Bassett).	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct. (Bassett).
50	41.10	32.39	24.06	17.45	11.79	55.80	45.69	35.24	26.54	17.75
100	46.73	38.01	29.04	20.78	13.61	64.80	54.09	42.39	31.89	21.05
200	52.49	44.94	32.17	23.40	15.61	72.81	64.40	47.29	36.41	24.52
400	57.89	47.09	35.93	26.45	17.64	82.18	67.72	53.04	41.32	27.50
800	....	50.45	39.22	28.38	....	....	72.85	58.10	44.71	....
1200	....	51.66	40.06	28.91	....	....	74.88	59.68	46.03	....



TABLE 66. — *Molecular conductivity of silver nitrate.* — Continued.

<i>v</i>	In a 75 p. ct. methyl alcohol, 25 p. ct. acetone mixture.		In a 50 p. ct. methyl alcohol, 50 p. ct. acetone mixture.		In a 25 p. ct. methyl alcohol, 75 p. ct. acetone mixture.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
50	40.45	53.81	38.46	45.94	25.49	28.40
100	46.36	64.24	48.31	61.69	33.67	37.78
200	55.60	73.65	58.22	68.61	42.42	47.00
400	63.98	83.08	67.87	83.88	51.50	59.87
800	65.62	92.69	77.83	100.90	63.19	75.12
1200	71.85	96.70	81.57	100.40	66.71	78.19
	Conductivity of solvent at $0^\circ = 1.3 \times 10^{-6}$ .		Conductivity of solvent at $0^\circ = 1.36 \times 10^{-6}$ .			

In methyl alcohol, acetone, and mixtures of these solvents.										
<i>v</i>	Percentage of acetone at $0^\circ$ .					Percentage of acetone at $25^\circ$ .				
	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
	50	41.10	40.45	38.46	25.49	....	55.80	53.81	45.94	28.40
100	46.73	46.36	48.31	33.67	....	64.80	64.24	61.69	37.78	....
200	52.49	55.60	58.22	42.42	8.18	72.81	73.65	68.61	47.00	10.36
400	57.89	63.98	67.87	51.50	8.58	72.18	83.08	83.88	59.87	11.57
800	....	65.62	77.83	63.19	9.64	....	92.69	100.90	75.12	12.08
1200	....	71.85	81.57	66.71	10.54	....	96.70	100.40	78.19	11.13

<i>v</i>	In a 75 p. ct. ethyl alcohol, 25 p. ct. acetone mixture.		In a 50 p. ct. ethyl alcohol, 50 p. ct. acetone mixture.		In a 25 p. ct. ethyl alcohol, 75 p. ct. acetone mixture.	
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$	$\mu_v 0^\circ$	$\mu_v 25^\circ$
50	15.86	22.39	16.91	21.42	13.38	16.36
100	19.90	28.38	22.13	28.12	17.42	23.06
200	25.06	33.64	25.72	33.64	22.20	27.60
400	27.40	39.82	33.55	43.49	29.80	....
800	31.51	46.30	40.51	53.51	37.84	45.80
1200	32.85	49.04	43.90	58.69	43.76	55.33
	Conductivity of solvent at $0^\circ = 2.4 \times 10^{-7}$ .		Conductivity of solvent at $0^\circ = 4.6 \times 10^{-7}$ .		Conductivity of solvent at $0^\circ = 4.4 \times 10^{-7}$ .	

In ethyl alcohol, acetone, and mixtures of these solvents.										
<i>v</i>	Percentage of acetone at $0^\circ$ .					Percentage of acetone at $25^\circ$ .				
	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct. (Bassett).	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
	50	11.79	15.86	16.91	13.38	....	17.75	22.39	21.42	16.36
100	13.61	19.90	22.13	17.42	....	21.05	28.38	28.12	23.06	....
200	15.61	25.06	25.72	22.20	8.18	24.52	33.64	33.64	27.60	10.36
400	17.64	27.40	33.55	29.80	8.58	27.50	39.82	43.49	....	11.57
800	....	31.51	40.51	37.84	9.64	....	46.30	53.51	45.80	12.08
1200	....	32.85	43.90	43.76	10.54	....	49.04	58.69	55.33	13.11

TABLE 67. — *Temperature coefficients of conductivity of silver nitrate.*

<i>v</i>	In water, acetone, and mixtures of these solvents, 0° to 25°.					In ethyl alcohol, acetone, and mixtures of these solvents, 0° to 25°.				
	0 p. ct. acetone.	25 p. ct. acetone.	50 p. ct. acetone.	75 p. ct. acetone.	100 p. ct. acetone.	0 p. ct. acetone.	25 p. ct. acetone.	50 p. ct. acetone.	75 p. ct. acetone.	100 p. ct. acetone.
50	0.0307	0.0409	0.0404	0.0289	....	0.0202	0.0165	0.0107	0.0089	....
100	.0334	.0400	.0411	.0294	....	.0189	.0170	.0108	.0130	....
200	.0329	.0409	.0430	.0299	0.0107	.0203	.0137	.0123	.0097	0.0107
400	.0314	.0416	.0424	.0305	.0139	.0224	.0181	.0118	....	.0139
800	.0309	.0416	.0429	.0300	.0101	....	.0188	.0128	.0084	.0101
1200	.0310	.0415	.0417	.0308	.0097	....	.0197	.0134	.0106	.0097

<i>v</i>	In methyl and ethyl alcohols, and mixtures of these solvents, 0° to 25°.					In methyl alcohol, acetone, and mixtures of these solvents, 0° to 25°.				
	0 p. ct. ethyl alcohol.	25 p. ct. ethyl alcohol.	50 p. ct. ethyl alcohol.	75 p. ct. ethyl alcohol.	100 p. ct. ethyl alcohol.	0 p. ct. acetone.	25 p. ct. acetone.	50 p. ct. acetone.	75 p. ct. acetone.	100 p. ct. acetone.
50	0.0143	0.0164	0.0186	0.0208	0.0202	0.0143	0.0132	0.0078	0.0046	....
100	.0155	.0169	.0184	.0214	.0189	.0143	.0154	.0119	.0049	....
200	.0155	.0173	.0188	.0222	.0203	.0155	.0130	.0071	.0068	0.0107
400	.0168	.0175	.0190	.0225	.0224	.0168	.0119	.0119	.0065	.0139
800	....	.0178	.0192	.0230	....	....	.0165	.0119	.0076	.0101
1200	....	.0180	.0196	.0237	....	....	.0138	.0092	.0069	.0097

Some of the values in table 66 are plotted as curves in figs. 42 and 43, the abscissæ representing the different percentages of acetone, and the ordinates the molecular conductivities. It will be seen that at 0°, for all dilutions but the lowest investigated, N/50, there is a pronounced point of inflection that appears in the 75 per cent acetone mixture. At 25° it has almost disappeared, but still manifests itself at the higher dilutions. The curves are almost identical in form with those obtained by Jones and Bingham<sup>1</sup> for calcium nitrate, in mixtures of the same solvents.

Table 67 shows that the temperature coefficients increase with the proportion of acetone up to the 50 per cent mixture, but a further increase in the proportion of acetone produces a rapid fall in the values for the temperature coefficients. With increase in concentration, the maximum value tends to shift to the 25 per cent acetone mixture. These results are also nearly identical with those obtained by Jones and Bingham with calcium nitrate.

The similarity of the curves (figs. 48 and 49), plotted from the values given in table 66, to the corresponding curves obtained by Jones and Bingham for calcium nitrate, is even more striking than in the case of the methyl alcohol and acetone mixtures. A pronounced maximum manifests itself at both 0° and 25°, appearing in the 25 per cent acetone mixture in the more concentrated solutions, and shifting, with increase in dilution, through the 50 per cent to the 75 per cent mixture.

<sup>1</sup> Amer. Chem. Journ., **34**, 481 (1905).

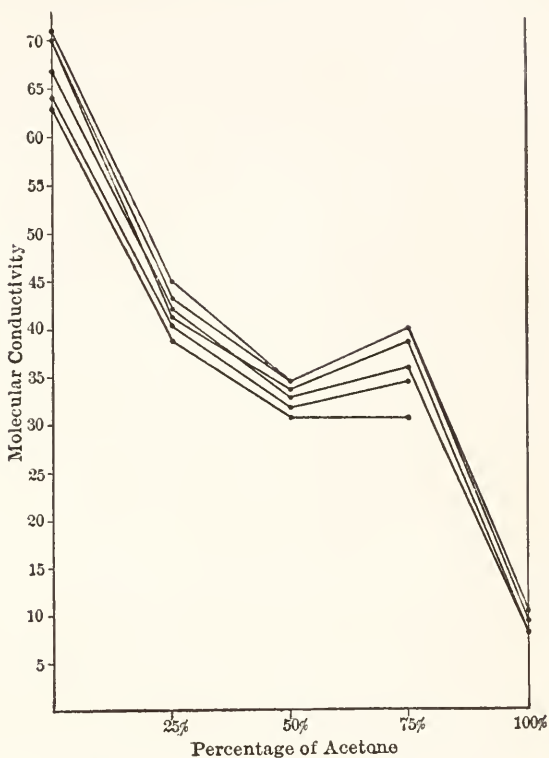


FIG. 42. — CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF WATER AND ACETONE AT 0°.

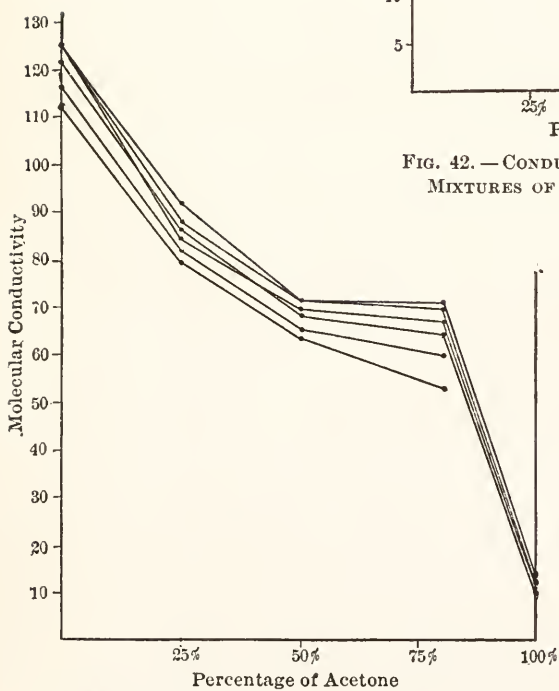


FIG. 43. — CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF WATER AND ACETONE AT 25°.

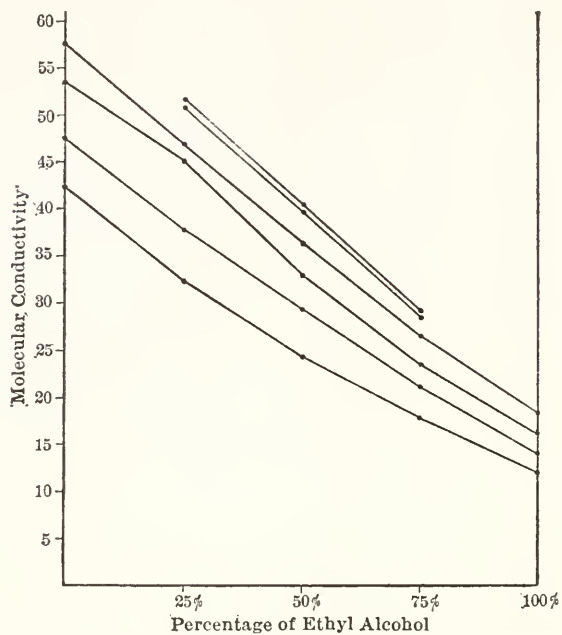


FIG. 44.—CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF METHYL AND ETHYL ALCOHOLS AT 0°.

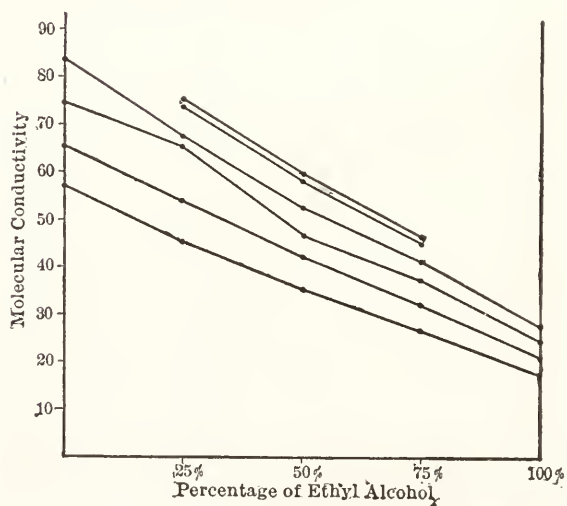


FIG. 45.—CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF METHYL AND ETHYL ALCOHOLS AT 25°.

As with calcium nitrate, the temperature coefficients (table 67) show a minimum in the 75 per cent mixture.

In view of the great similarity in conductivity phenomena exhibited by silver and calcium nitrates, in mixtures of water and of methyl and ethyl

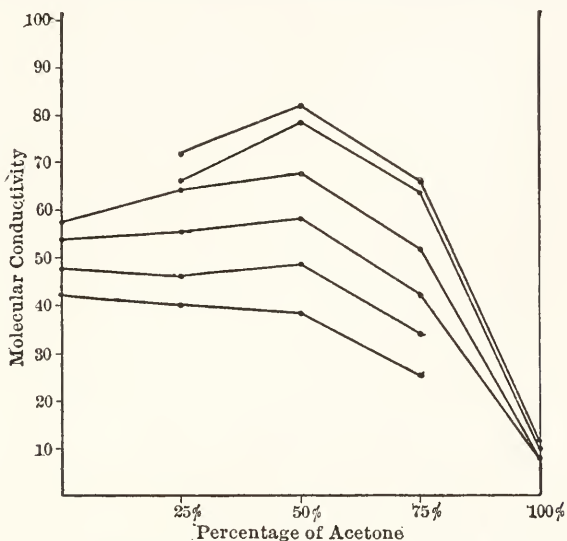


FIG. 46. — CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF METHYL ALCOHOL AND ACETONE AT 0°.

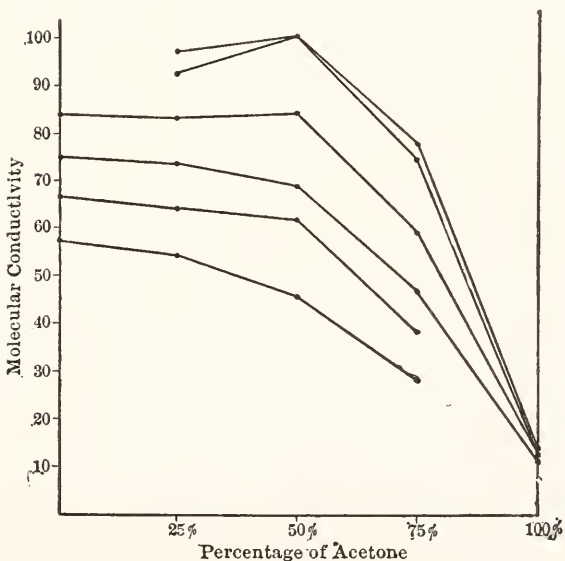


FIG. 47. — CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF METHYL ALCOHOL AND ACETONE AT 25°.

alcohols with acetone, it is interesting to know whether this is also true of solutions of the two salts in mixtures of water with the alcohols. By comparing the values for calcium nitrate in these mixtures, obtained by Jones

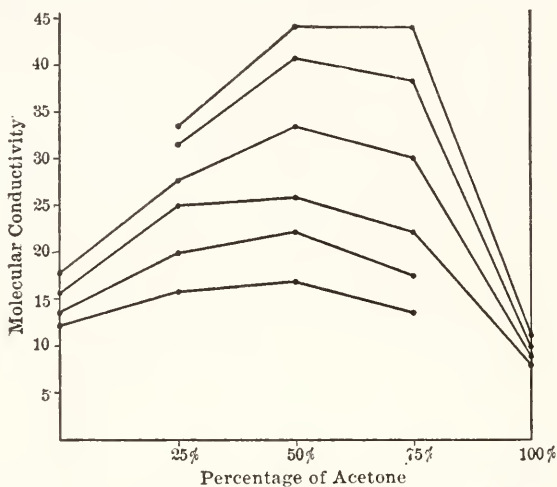


FIG. 48.—CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF ETHYL ALCOHOL AND ACETONE AT 0°.

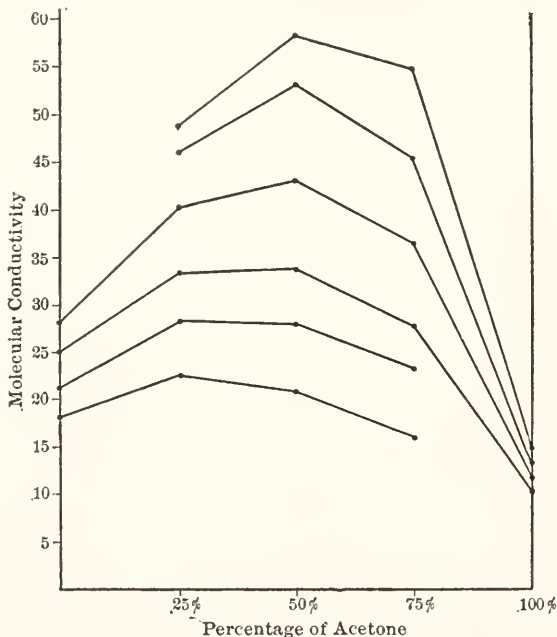


FIG. 49.—CONDUCTIVITY OF SILVER NITRATE IN MIXTURES OF ETHYL ALCOHOL AND ACETONE AT 25°.

and Carroll,<sup>1</sup> with the corresponding values for the silver salt which had been obtained by Jones and Bassett, it is seen that in mixtures of ethyl alcohol with water the conductivity curves for both salts are of the same form, showing no marked minimum, but exhibiting a tendency towards one in the 75 per cent alcohol mixture. In mixtures of methyl alcohol with water, however, while silver nitrate gives a very marked minimum in the 50 per cent mixture, the calcium salt does not. Jones and Carroll did not work with dilutions greater than N/256, and it is quite possible that more dilute solutions would show a minimum.

Tables 66 and 67 (figs. 44 and 45) show that there is no trace of either a maximum or minimum, the curves being straight lines to within the limits of experimental error. The temperature coefficients (table 67) increase regularly with the proportion of ethyl alcohol up to the 75 per cent mixture, and then remain practically constant, showing a slight tendency to drop.

A study of table 66 (figs. 46 and 47) shows that at 0°, at the higher dilutions, silver nitrate in mixtures of methyl alcohol and acetone gives a maximum that almost disappears at 25°, although still evident in the more dilute solutions. The maximum appears in the 50 per cent mixture. Here again the results are very similar to those found for calcium nitrate by Jones and Bingham, although silver nitrate does not, like the calcium salt, show, within the limits of the dilutions investigated, any maximum in the 25 per cent acetone mixture.

The temperature coefficients (table 67) exhibit a pronounced maximum in the 75 per cent acetone mixture. This applies equally well to calcium nitrate.

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<sup>1</sup> Amer. Chem. Journ., **32**, 521 (1904).

## WORK OF McMASTER.

### EXPERIMENTAL.

#### APPARATUS.

#### CONDUCTIVITY.

The Kohlrausch method of measuring conductivity, with a Wheatstone bridge, telephone receiver, and induction coil, was employed. The bridge-wire was of "manganin" and was calibrated before beginning the work by the method of Strouhal and Barus.<sup>1</sup>

The resistance coils were carefully calibrated.

The conductivity cells were of the form used by Jones and Bingham.<sup>2</sup> In order to work with the alcohols and acetone, it was necessary to use cells of this form. They were made of hard glass, with ground-glass stoppers. The glass tubes carrying the platinum electrodes were sealed into both the upper and lower walls of the stopper. By using such cells, the presence of rubber or wax, which would be dissolved by the solvent, was avoided. They also prevent evaporation of the more volatile solvents, and protect the anhydrous alcohols and acetone from the moisture of the baths and air.

The electrodes were treated in the manner recommended by Whetham.<sup>3</sup> They were first coated with platinum black and then heated in the flame of a blast-lamp. Electrodes covered with platinum black absorb a small amount of salt from the solution, and give up some of it again when water or a more dilute solution is placed in the cell. The gray platinum formed by the heating process does not absorb an appreciable amount of salt, and the oxidizing action of platinum black is also avoided by this treatment.

The zero-bath consisted of an inner and outer vessel. The inner vessel and the space between the two were filled with finely crushed, pure ice, moistened with distilled water. The 25° bath was of the usual form, the stirrer being driven by means of a hot-air engine, or a Rabe water turbine. The Ostwald thermoregulator was used. The thermometers employed were accurate to a tenth of a degree. Burettes and flasks were carefully calibrated, according to the method of Morse and Blalock.<sup>4</sup>

#### VISCOSITY.

The apparatus used was of exactly the form described by Ostwald and Luther.<sup>5</sup> A fixed volume of the liquid, the viscosity of which was to be

<sup>1</sup> Wied. Ann., **10**, 326 (1880).

<sup>2</sup> Amer. Chem. Journ., **34**, 493 (1905).

<sup>3</sup> Phil. Trans., **94A**, 321 (1900).

<sup>4</sup> Amer. Chem. Journ., **16**, 479 (1894).

<sup>5</sup> Physiko-Chemische Messungen, II. Aufl., p. 260.



measured, was introduced into the viscometer. The liquid was raised to the mark above the bulb by means of air-pressure, the air being dried with calcium chloride or with concentrated sulphuric acid. The pressure was then released by means of a Mohr pinchcock on a thick-walled rubber tube. The time of flow through the capillary tube was determined by means of a stop-watch, reading to two-tenths of a second.

In order to calculate the viscosity, it is necessary to measure the specific gravity of the solution. For this purpose we used the pycnometer employed by Jones and Bingham<sup>1</sup> in their work. The pycnometer was so constructed as to allow the large expansion of the alcohols and acetone, and avoid loss by evaporation.

A large battery-jar, filled with finely crushed ice moistened with water, was used for the zero-bath. The ice was frequently renewed to keep the temperature constant. For the 25° bath a beaker holding 5 liters was employed. The bath was stirred by means of a hot-air engine, the temperature being kept at 25°. It did not vary more than a tenth of a degree.

#### SOLVENTS.

##### WATER.

The water used in this work was purified according to the following method: Ordinary distilled water was first distilled from potassium dichromate and sulphuric acid. This water was redistilled from acidified potassium dichromate and then from barium hydroxide. Water thus purified gave a conductivity of  $1 \times 10^{-6}$  at 0° and from  $1.5$  to  $2.0 \times 10^{-6}$  at 25°.

##### METHYL ALCOHOL.

The methyl alcohol used was the best commercial article that could be obtained. It was first boiled with calcium oxide for several days, then distilled and allowed to stand over anhydrous copper sulphate for weeks. Before use it was distilled from the copper sulphate, using a Linnemann fractionating head. Care was always taken to keep it free from moisture. The first and last portions of the distillate were discarded. The mean value of the conductivity was  $1.1 \times 10^{-6}$  at 0° and  $2 \times 10^{-6}$  at 25°.

##### ETHYL ALCOHOL.

The ethyl alcohol was the best article commercially obtainable, and was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of  $0.6 \times 10^{-6}$  at 0° and  $1.5 \times 10^{-6}$  at 25°.

##### ACETONE.

The acetone was dried over fused calcium chloride for weeks, and distilled with a Linnemann fractionating head. Its conductivity was  $0.4 \times 10^{-6}$  at 0° and  $0.6 \times 10^{-6}$  at 25°.

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<sup>1</sup> Amer. Chem. Journ., **34**, 495 (1905).

## SOLUTIONS.

In making up mixtures of solvents,  $x$  c. c. of an alcohol or of acetone were diluted to 100 c. c. Such a solution was designated as a mixture of " $x$  per cent alcohol" or " $x$  per cent acetone." Since acetone has a large coefficient of expansion, it was necessary to make up the mixtures at the same temperature (18°). The alcohol or acetone was always brought to this temperature before making up the mixture.

In making up the mother-solution the exact amount of the salt was weighed into a measuring-flask and, after addition of a portion of the solvent, the substance was dissolved and the flask filled to the mark. Since heat was generated and there was a rise in temperature, the solution was brought to the designated temperature before diluting to the mark. The various concentrations were obtained by successive dilution, the mother-solutions being the starting-point. Where the quantity to be used was too small to be measured with accuracy, one of the intermediate solutions was taken as a starting-point for further dilution.

## CONDUCTIVITY MEASUREMENTS.

In all determinations of conductivity from 3 to 5 different resistances were used. The values for the molecular conductivity ( $\mu_v$ ), given in the tables, are, therefore, the mean of several determinations. The determination of the cell constants was carried out by the method employed by Jones and West.<sup>1</sup> Cells calibrated in this manner gave very accurate results. The constants were checked at frequent intervals. After being used the cells were not allowed to remain in contact with the solution, since small quantities of salt are absorbed by the electrodes. They were allowed to remain empty after being dried out with alcohol and ether, since acetic acid is formed by the action of the platinum on the alcohol and ether in the presence of air, but they were always filled with pure distilled water when not in use for any appreciable time.

Solutions of potassium chloride, N/50 and N/500, were used in determining the cell constants. The conductivity of the former was taken as 129.7 at 25°; 136.5 at 25° being taken as the value of  $\mu_v$  for the N/500 solution of potassium chloride.

In the following tables  $v$ =number of liters of solution containing a gram-molecular weight of the salt;  $\mu_v 0^\circ$ =molecular conductivity at 0°;  $\mu_v 25^\circ$ =molecular conductivity at 25°. The temperature coefficients are obtained by dividing the increase in the conductivity per degree by the conductivity at the lower temperature. The expression that was applied is—

$$\frac{\mu_v 25^\circ - \mu_v 0^\circ}{25} \cdot \frac{1}{\mu_v 0^\circ}$$

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<sup>1</sup> Amer. Chem. Journ., 34, 357 (1905).

## LITHIUM BROMIDE.

The lithium bromide used in this work was obtained from Kahlbaum. No appreciable impurity could be detected. It was dried in an air-bath at 159°, after which it was kept in a desiccator. Whenever the salt was exposed to the air, the operation of drying to constant weight was repeated.

TABLE 68. — *Conductivity of lithium bromide at 0° and 25°.*

$v$	In water.			In a mixture of 25 p. ct. methyl alcohol and water.			In a mixture of 50 p. ct. methyl alcohol and water.		
	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.
2	42.09	76.17	.0324	24.46	49.86	.0415	18.42	37.01	0.0404
5	45.33	83.33	.0335	26.57	54.90	.0426	20.57	41.58	.0408
10	47.25	86.09	.0329	27.52	57.46	.0435	21.71	43.99	.0410
50	51.43	95.62	.0344	30.04	63.69	.0448	24.24	49.46	.0416
100	51.92	96.41	.0342	30.50	64.78	.0450	24.40	50.27	.0424
200	53.27	99.51	.0347	31.24	66.25	.0448	25.16	51.74	.0423
400	53.71	100.34	.0347	31.65	66.65	.0442	25.96	53.24	.0420
800	55.45	104.81	.0356	32.87	68.83	.0438	26.42	54.48	.0425
1600	56.12	106.23	.0357	33.07	69.24	.0437	26.91	55.15	.0420

$v$	In a mixture of 75 p. ct. methyl alcohol and water.			In methyl alcohol.			In a mixture of 25 p. ct. ethyl alcohol and water.		
	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.
2	19.51	33.66	0.0290	22.02	31.35	0.0169	17.82	41.21	0.0525
5	21.67	38.31	.0307	30.55	42.57	.0157	18.92	45.03	.0552
10	23.50	41.99	.0314	35.92	50.21	.0159	19.66	47.05	.0557
50	27.05	48.68	.0320	46.48	64.92	.0159	21.60	52.52	.0572
100	27.73	49.98	.0321	49.36	69.19	.0161	21.67	52.58	.0570
200	28.92	52.29	.0323	52.51	73.62	.0161	22.09	54.37	.0584
400	29.55	53.56	.0325	55.18	78.25	.0167	22.50	54.41	.0567
800	30.22	55.29	.0332	57.45	82.56	.0175	24.51	56.46	.0521
1600	31.35	57.59	.0335	57.63	83.64	.0181	25.72	57.10	.0448

$v$	In a mixture of 50 p. ct. ethyl alcohol and water.			In a mixture of 75 p. ct. ethyl alcohol and water.			In ethyl alcohol.		
	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.	$\mu_{v0^\circ}$	$\mu_{v25^\circ}$	Temperature coefficient.
2	11.70	27.50	0.0540	9.20	18.96	0.0424	6.11	10.18	0.0266
5	12.48	29.51	.0546	10.55	22.11	.0438	8.67	14.00	.0246
10	12.62	31.41	.0595	11.59	24.26	.0437	10.55	17.22	.0253
50	13.71	35.41	.0633	11.87	25.62	.0463	14.40	23.28	.0247
100	13.98	36.12	.0633	12.14	26.29	.0466	15.69	25.57	.0252
200	14.34	37.26	.0639	12.77	27.66	.0466	17.29	28.26	.0254
400	14.96	38.39	.0626	13.13	28.62	.0472	18.55	30.32	.0254
800	15.77	39.94	.0613	13.62	29.78	.0474	19.71	31.73	.0244
1600	16.06	40.01	.0596	13.83	29.91	.0465	20.79	33.36	.0242

TABLE 68.—*Conductivity of lithium bromide at 0° and 25°.*—Continued.

$\nu$	In a mixture of 25 p. ct. methyl alcohol and ethyl alcohol.			In a mixture of 50 p. ct. methyl alcohol and ethyl alcohol.			In a mixture of 75 p. ct. methyl alcohol and ethyl alcohol.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
2	8.59	13.51	0.0229	12.22	18.37	0.0201	16.46	24.22	0.0188
5	12.55	19.08	.0208	17.38	25.54	.0188	23.34	33.38	.0172
10	15.17	22.97	.0206	21.03	30.72	.0184	27.71	39.60	.0171
50	21.07	31.56	.0199	28.69	41.81	.0183	37.02	52.80	.0170
100	22.70	34.55	.0209	30.42	44.48	.0185	38.96	55.92	.0174
200	24.50	37.61	.0214	32.95	48.86	.0193	41.64	60.03	.0176
400	26.08	40.03	.0214	34.76	51.31	.0190	44.21	63.76	.0177
800	26.94	41.82	.0221	35.83	53.29	.0195	46.51	66.73	.0174
1600	29.08	45.07	.0220	37.53	55.74	.0194	49.57	71.37	.0176

$\nu$	In a mixture of 25 p. ct. acetone and water.			In a mixture of 50 p. ct. acetone and water.			In a mixture of 75 p. ct. acetone and water.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
5	27.58	56.23	0.0415	20.37	41.82	0.0421	17.40	31.47	0.0323
10	28.82	59.71	.0429	21.70	45.16	.0432	20.40	36.49	.0315
50	31.49	65.64	.0434	24.81	51.95	.0437	25.76	46.77	.0326
100	31.60	65.82	.0433	25.03	52.46	.0438	27.29	49.87	.0331
200	32.29	67.88	.0441	26.10	54.64	.0437	28.87	52.87	.0332
400	32.98	68.69	.0433	26.81	56.44	.0442	30.10	55.53	.0338
800	35.18	70.25	.0399	27.07	57.54	.0430	30.20	56.46	.0348
1600	35.70	71.47	.0401	28.34	59.28	.0437	31.65	61.10	.0372

$\nu$	In acetone.			In a mixture of 25 p. ct. acetone and methyl alcohol.			In a mixture of 50 p. ct. acetone and methyl alcohol.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
5	9.35	10.82	0.00629	29.65	40.04	0.0140	27.99	35.37	0.0105
10	11.91	14.08	.00729	35.03	47.57	.0143	34.27	42.32	.00939
50	22.36	26.77	.00789	46.71	63.44	.0143	48.65	61.77	.0108
100	28.86	34.52	.00784	49.68	67.40	.0142	52.67	68.29	.0118
200	37.33	47.45	.01080	53.28	73.81	.0154	57.69	74.13	.0114
400	48.28	57.96	.00802	56.45	78.11	.0153	61.74	79.77	.0117
800	59.42	72.16	.00858	58.91	81.55	.0154	64.70	85.57	.0129
1600	70.89	85.90	.00847	60.38	83.53	.0153	67.02	89.45	.0134

$\nu$	In a mixture of 75 p. ct. acetone and methyl alcohol.			In a mixture of 25 p. ct. acetone and ethyl alcohol.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
5	23.36	30.06	0.0115	11.80	16.94	0.0174
10	29.77	38.15	.0112	14.72	20.91	.0168
50	48.45	61.89	.0111	21.70	31.00	.0171
100	55.00	70.87	.0115	23.70	34.38	.0180
200	62.74	80.63	.0114	26.38	38.27	.0180
400	72.25	91.17	.0105	28.28	41.74	.0190
800	82.20	100.28	.0088	28.88	42.97	.0195
1600	84.15	106.14	.0104	29.21	44.24	.0206

TABLE 68.—*Conductivity of lithium bromide at 0° and 25°.*—Continued.

$\nu$	In a mixture of 50 p. ct. acetone and ethyl alcohol.			In a mixture of 75 p. ct. acetone and ethyl alcohol.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
5	14.70	19.38	0.0122	14.48	18.07	0.00992
10	19.23	25.75	.0135	19.16	23.23	.00850
50	30.25	39.36	.0120	33.20	40.08	.00829
100	34.50	45.12	.0123	39.32	48.94	.00978
200	39.20	52.76	.0138	47.31	58.01	.00905
400	43.83	59.26	.0141	55.55	68.28	.00917
800	46.92	64.33	.0148	61.20	77.57	.01070
1600	50.98	71.22	.0159	66.28	83.36	.01030

TABLE 69.—*Comparison of the conductivities of lithium bromide.*

$\nu$	In mixtures of methyl alcohol and water at 0° and at 25°.									
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
2	42.09	24.46	18.42	19.51	22.02	76.17	49.86	37.01	33.66	31.35
5	45.33	26.57	20.57	21.67	30.55	83.33	54.90	41.58	38.31	42.57
10	47.25	27.52	21.71	23.50	35.92	86.09	57.46	43.99	41.99	50.21
50	51.43	30.04	24.24	27.05	46.48	95.62	63.69	49.46	48.68	64.92
100	51.92	30.50	24.40	27.73	49.36	96.41	64.78	50.27	49.98	69.19
200	53.27	31.24	25.16	28.92	52.51	99.51	66.25	51.74	52.29	73.62
400	53.71	31.65	25.96	29.55	55.18	100.34	66.65	53.24	53.56	78.25
800	55.45	32.87	26.42	30.22	57.45	104.81	68.83	54.48	55.29	82.56
1600	56.12	33.07	26.91	31.35	57.63	106.23	69.24	55.15	57.59	83.64

$\nu$	In mixtures of ethyl alcohol and water at 0° and at 25°.									
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
2	42.09	17.82	11.70	9.20	6.11	76.17	41.21	27.50	18.96	10.18
5	45.33	18.92	12.48	10.55	8.67	83.83	45.03	29.51	22.11	14.00
10	47.25	19.66	12.62	11.59	10.55	86.09	47.05	31.41	24.26	17.22
50	51.43	21.60	13.71	11.87	14.40	95.62	52.52	35.41	25.62	23.28
100	51.92	21.67	13.98	12.14	15.69	96.41	52.58	36.12	26.29	25.57
200	53.27	22.09	14.34	12.77	17.29	99.51	54.37	37.26	27.66	28.26
400	53.71	22.50	14.96	13.13	18.55	100.34	54.41	38.39	28.62	30.32
800	55.45	24.51	15.77	13.62	19.71	104.81	56.46	39.94	29.78	31.73
1600	56.12	25.72	16.06	13.83	20.79	106.23	57.10	40.01	29.91	33.36

$\nu$	In mixtures of methyl alcohol and ethyl alcohol at 0° and at 25°.									
	C <sub>2</sub> H <sub>5</sub> OH	25 p. ct. CH <sub>3</sub> OH	50 p. ct. CH <sub>3</sub> OH	75 p. ct. CH <sub>3</sub> OH	CH <sub>2</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	25 p. ct. CH <sub>3</sub> OH	50 p. ct. CH <sub>3</sub> OH	75 p. ct. CH <sub>3</sub> OH	CH <sub>3</sub> OH
2	6.11	8.59	12.22	16.46	22.02	10.18	13.51	18.37	24.22	31.35
5	8.67	12.55	17.38	23.34	30.55	14.00	19.08	25.54	33.38	42.57
10	10.55	15.17	21.03	27.71	35.92	17.22	22.97	30.72	39.60	50.21
50	14.40	21.07	28.69	37.02	46.48	23.28	31.56	41.81	52.80	64.92
100	15.69	22.70	30.42	38.96	49.36	25.57	34.55	44.48	55.92	69.19
200	17.27	24.50	32.95	41.64	52.51	28.26	37.61	48.86	60.03	73.62
400	18.55	26.08	34.76	44.21	55.18	30.32	40.03	51.31	63.76	78.25
800	19.71	26.94	35.83	46.51	57.45	31.73	41.82	53.29	66.73	82.56
1600	20.79	29.08	37.53	49.57	57.63	33.36	45.07	55.74	71.37	83.64

TABLE 69.—*Comparison of the conductivities of lithium bromide.*—Continued.

<i>v</i>	In mixtures of acetone and water at 0°.					In mixtures of acetone and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	45.33	27.58	20.37	17.40	9.35	83.33	56.23	41.82	31.47	10.82
10	47.25	28.82	21.70	24.00	11.91	86.09	59.71	45.16	36.49	14.80
50	51.43	31.49	24.81	25.76	22.36	95.61	65.64	51.95	46.77	26.77
100	51.92	31.60	25.03	27.29	28.86	96.41	65.82	52.46	49.87	34.52
200	53.27	32.29	26.10	28.87	37.33	99.51	67.88	54.64	52.87	47.45
400	53.71	32.98	26.81	30.10	48.28	100.34	68.69	56.44	55.53	57.96
800	55.45	35.18	27.07	30.20	59.42	104.81	70.25	57.54	56.46	72.16
1600	56.12	35.71	28.34	31.65	70.89	106.23	71.47	59.28	61.10	85.90

<i>v</i>	In mixtures of acetone and methyl alcohol at 0° and at 25°.									
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	30.55	29.65	27.99	23.36	9.35	42.57	40.04	35.37	30.06	10.82
10	35.92	35.03	34.27	29.77	11.91	50.21	47.57	42.32	38.15	14.08
50	46.48	46.71	48.65	48.45	22.36	64.92	63.44	61.77	61.89	26.77
100	49.36	49.68	52.67	55.00	28.86	69.19	67.40	68.29	70.87	34.52
200	52.51	53.28	57.69	62.74	37.33	73.62	73.81	74.13	80.63	47.45
400	55.18	56.45	61.74	72.25	48.28	78.25	78.11	79.77	91.17	57.96
800	57.45	58.91	64.70	82.20	59.42	82.56	81.55	85.57	100.28	72.16
1600	57.63	60.38	67.02	84.15	70.89	83.64	83.53	89.45	106.14	85.90

<i>v</i>	In mixtures of acetone and ethyl alcohol at 0° and at 25°.									
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	8.67	11.80	14.70	14.48	9.35	14.00	16.94	19.38	18.07	10.82
10	10.55	14.72	19.23	19.16	11.91	17.22	20.91	25.75	23.23	14.08
50	14.40	21.70	30.25	33.20	22.36	23.28	31.00	39.36	40.08	26.77
100	15.69	23.70	34.50	39.32	28.86	25.57	34.38	45.12	48.94	34.52
200	17.29	26.38	39.20	47.31	37.33	28.26	38.27	52.76	58.01	47.45
400	18.55	28.28	43.83	55.55	48.28	30.32	41.74	59.26	68.28	57.96
800	19.71	28.88	46.92	61.20	59.42	31.73	42.97	64.33	77.57	72.16
1600	20.79	29.21	50.98	66.28	70.89	33.36	44.24	71.22	83.36	85.90

TABLE 70.—*Comparison of the temperature coefficients of conductivity of lithium bromide from 0° to 25°.*

<i>v</i>	In mixtures of methyl alcohol and water.					In mixtures of ethyl alcohol and water.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
2	0.0324	0.0415	0.0404	0.0290	0.0169	0.0324	0.0525	0.0540	0.0424	0.0266
5	.0335	.0426	.0408	.0307	.0157	.0335	.0552	.0546	.0438	.0246
10	.0329	.0435	.0410	.0314	.0159	.0329	.0557	.0595	.0437	.0253
50	.0344	.0448	.0416	.0320	.0159	.0344	.0572	.0633	.0463	.0247
100	.0342	.0450	.0424	.0321	.0161	.0342	.0570	.0633	.0466	.0252
200	.0347	.0448	.0423	.0323	.0161	.0347	.0584	.0639	.0466	.0254
400	.0347	.0442	.0420	.0325	.0167	.0347	.0567	.0626	.0472	.0254
800	.0356	.0438	.0425	.0332	.0175	.0356	.0521	.0613	.0474	.0244
1600	.0357	.0437	.0420	.0335	.0181	.0357	.0448	.0596	.0465	.0242

TABLE 70.—*Comparison of the temperature coefficients of conductivity of lithium bromide from 0° to 25°.—Continued.*

$\nu$	In mixtures of methyl alcohol and ethyl alcohol.					In mixtures of acetone and water.				
	C <sub>2</sub> H <sub>5</sub> OH	25 p. ct. CH <sub>3</sub> OH	50 p. ct. CH <sub>3</sub> OH	75 p. ct. CH <sub>3</sub> OH	CH <sub>3</sub> OH	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
2	0.0266	0.0229	0.0201	0.0188	0.0169	.....	.....	.....	.....	.....
5	.0246	.0208	.0188	.0172	.0157	0.0335	0.0415	0.0421	0.0323	0.00629
10	.0253	.0206	.0184	.0171	.0159	.0329	.0429	.0432	.0315	.00729
50	.0247	.0199	.0183	.0170	.0159	.0344	.0434	.0437	.0326	.00789
100	.0252	.0209	.0185	.0174	.0161	.0342	.0433	.0438	.0331	.00784
200	.0254	.0214	.0193	.0176	.0161	.0347	.0441	.0437	.0332	.01080
400	.0254	.0214	.0190	.0177	.0167	.0347	.0433	.0442	.0338	.00802
800	.0244	.0221	.0195	.0174	.0175	.0356	.0399	.0430	.0348	.00858
1600	.0242	.0220	.0194	.0176	.0181	.0357	.0401	.0437	.0372	.00847

$\nu$	In mixtures of acetone and methyl alcohol.					In mixtures of acetone and ethyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
5	0.0157	0.0140	0.0105	0.0115	0.00629	0.0246	0.0174	0.0122	0.00992	0.00629
10	.0159	.0143	.00939	.0112	.00729	.0253	.0168	.0135	.00850	.00729
50	.0159	.0143	.0108	.0111	.00789	.0247	.0171	.0120	.00829	.00789
100	.0161	.0142	.0118	.0115	.00784	.0252	.0180	.0123	.00978	.00784
200	.0161	.0154	.0114	.0114	.01080	.0254	.0180	.0138	.00905	.01080
400	.0167	.0153	.0117	.0105	.00802	.0254	.0190	.0141	.00917	.00802
800	.0175	.0154	.0129	.0088	.00858	.0244	.0195	.0148	.01070	.00858
1600	.0181	.0153	.0134	.0104	.00847	.0242	.0206	.0159	.01030	.00847

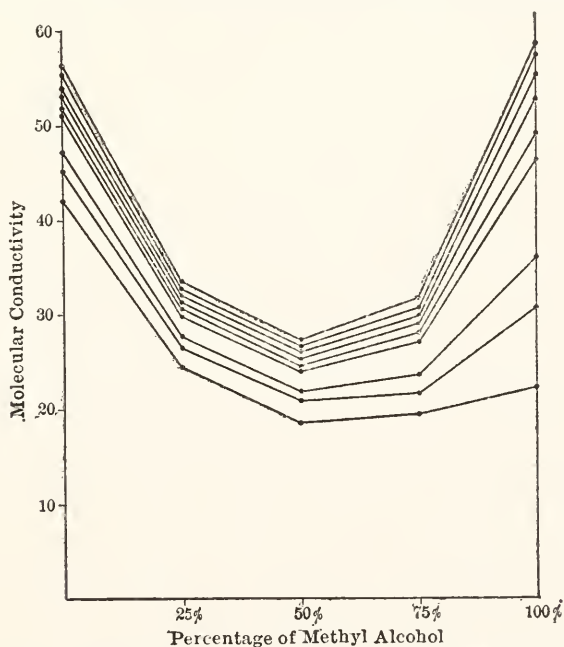


FIG. 50.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 0°.

Table 68 (figs. 50 and 51) shows that lithium bromide, in mixtures of methyl alcohol and water, gives a pronounced minimum in conductivity. The minimum is more marked at 0° than at 25°. At 25° the minimum occurs in the 75 per cent mixture up to  $v = 100$ . Beyond this dilution the minimum occurs solely in the 50 per cent mixture. At 0° the minimum appears in the 50 per cent mixture alone. We also notice that at 0° the values of  $\mu_v$  for the pure methyl alcohol at the higher dilutions exceed the values of  $\mu_v$  for the corresponding aqueous solutions. These points will be made clear by a study of the figures. In all cases the curves represent the molecular conductivities at the successive dilutions.

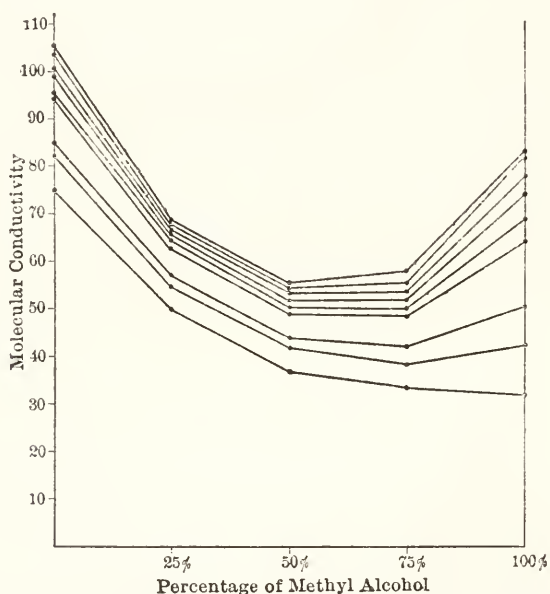


FIG. 51. — CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 25°.

The temperature coefficients of conductivity increase with the dilution, and they are also greater in the mixtures than in the pure solvents, the maximum appearing in the 25 per cent mixture. The temperature coefficients of conductivity of salts in water generally increase with the dilution, as Jones<sup>1</sup> has pointed out in a recent article.

Table 68 (figs. 52 and 53) shows that lithium bromide, in mixtures of ethyl alcohol and water, also gives a minimum in conductivity. At high concentrations the minimum does not appear, either at 0° or at 25°. At

<sup>1</sup> Amer. Chem. Journ., **35**, 445 (1906).



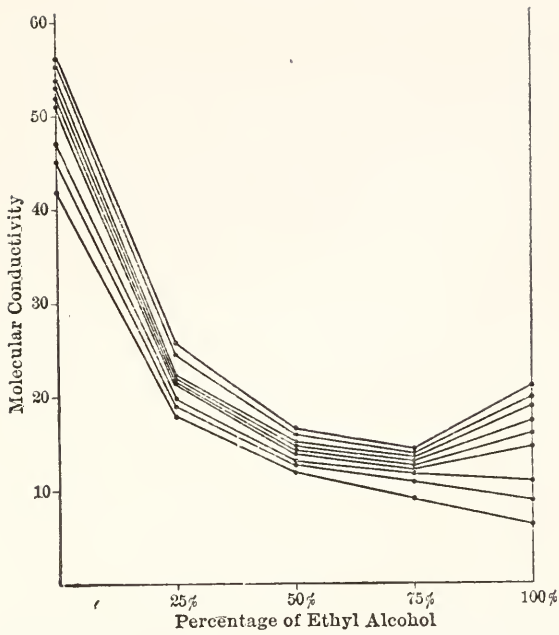


FIG. 52.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 0°.

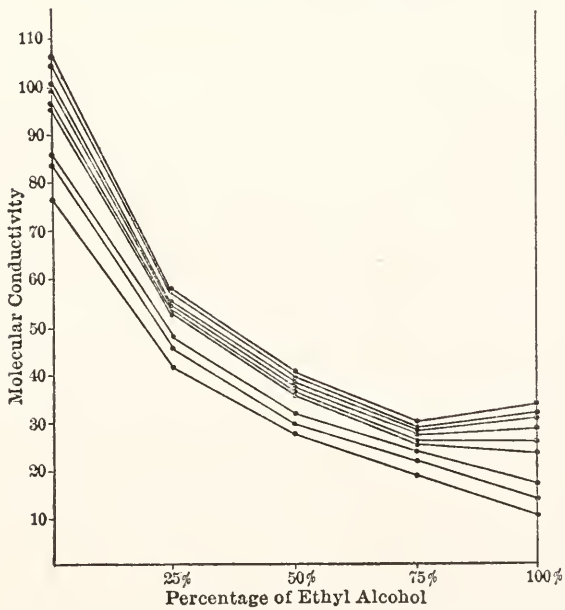


FIG. 53.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°.

both temperatures the minimum appears only in the 75 per cent mixture. At 0° the minimum begins with  $v = 50$ ; at 25° it begins at  $v = 200$ . It is to be noticed that the minimum is more marked at the lower temperature, being very slight at 25°.

The temperature coefficients in ethyl alcohol are almost constant. This same fact was found by Jones and Bingham<sup>1</sup> in the case of calcium nitrate. The temperature coefficients are greater in the mixtures than in the pure solvents, the maximum appearing in the 50 per cent mixture.

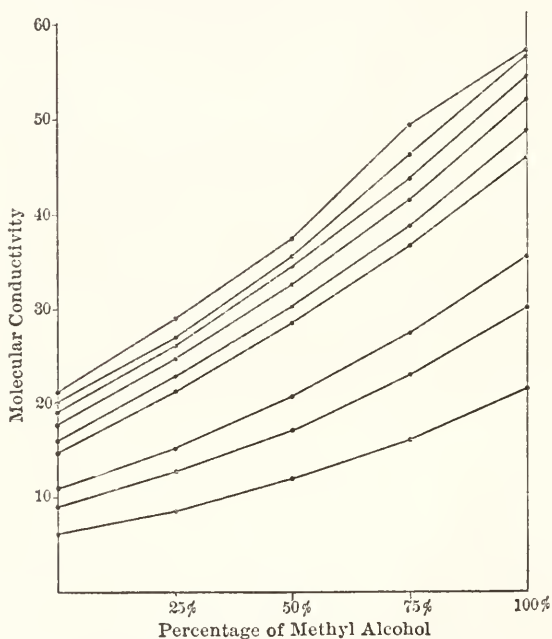


FIG. 54.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 0°.

Tables 68 and 69 (figs. 54 and 55) show that lithium bromide, in mixtures of methyl and ethyl alcohols, gives no minimum in conductivity. In fact, the conductivity values for the solutions in the mixed solvent approach the mean value of the conductivities in the pure solvents. The conductivity curves at the high concentrations show a slight sagging at both temperatures, but beyond  $v = 50$  the curves are nearly straight lines. This same fact has been observed by others working with mixtures of methyl and ethyl alcohols. The temperature coefficients obey, approximately, the law of averages.

<sup>1</sup> Amer. Chem. Journ., 34, 529 (1905).

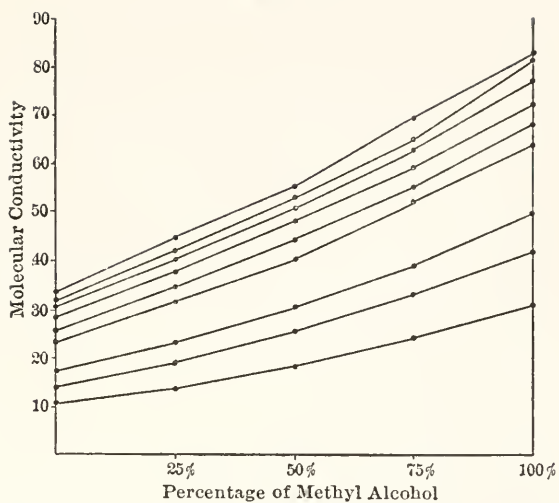


FIG. 55.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 25°.

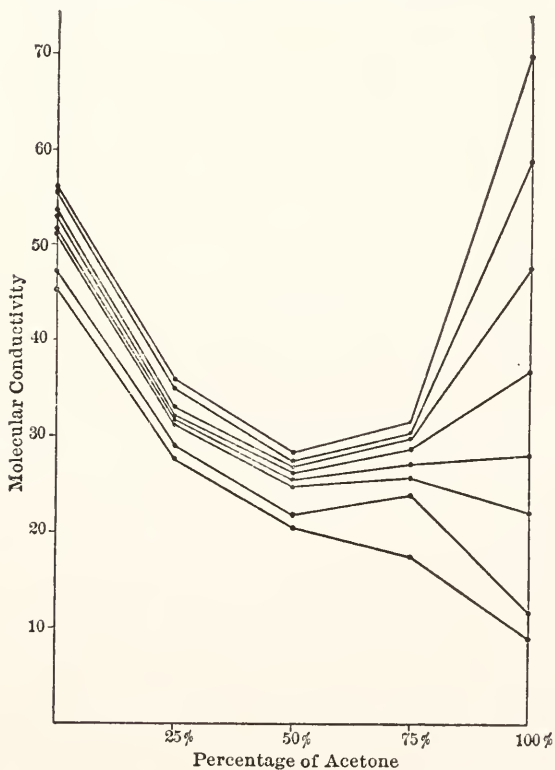


FIG. 56.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ACETONE AND WATER AT 0°.

Table 68 (figs. 56 and 57), for lithium bromide in mixtures of acetone and water, gives the minimum which is exhibited in mixtures of the alcohols and water under similar circumstances. The minimum is more marked at the lower temperature. The curves diverge from each other rapidly between the 75 per cent mixture and pure acetone at both temperatures. This seems to indicate that the addition of small amounts of water greatly increases the dissociation. It is also to be noticed that, at the lower temperature, the values of  $\mu_w$  for the pure acetone at the higher dilutions exceed those of  $\mu_w$  for the corresponding aqueous solutions. A similar phenomenon was noticed in the solution in methyl alcohol and water.

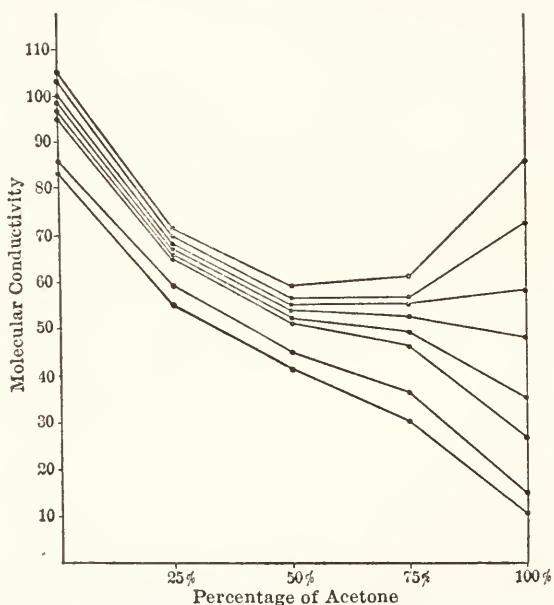


FIG. 57. — CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ACETONE AND WATER AT 25°.

In pure acetone the temperature coefficients increase with the dilution. In the mixtures the increase is very small.

Tables 69 and 70 (figs. 58 and 59), for lithium bromide in mixtures of acetone and methyl alcohol, give a maximum in conductivity in the 75 per cent mixture at both temperatures. The maximum is increased by rise in temperature. This same phenomenon was found by Jones and Bingham, working with lithium nitrate in mixtures of acetone and methyl alcohol. It will be recalled that we obtained a minimum conductivity with this salt in mixtures of the alcohols and water.

Tables 69 and 70 (figs. 60 and 61), for lithium bromide in mixtures of acetone and ethyl alcohol, show the same characteristics as were observed in the tables for this salt in mixtures of acetone and methyl alcohol. The values for  $\mu_v$  in acetone are greater than the corresponding values in the pure ethyl alcohol at practically all dilutions.

#### CONDUCTIVITY AND VISCOSITY OF CERTAIN SALTS.

The temperature coefficients increase slightly with the increase in dilution. The values are highest in ethyl alcohol, from which there is a regular gradation to the values of pure acetone.

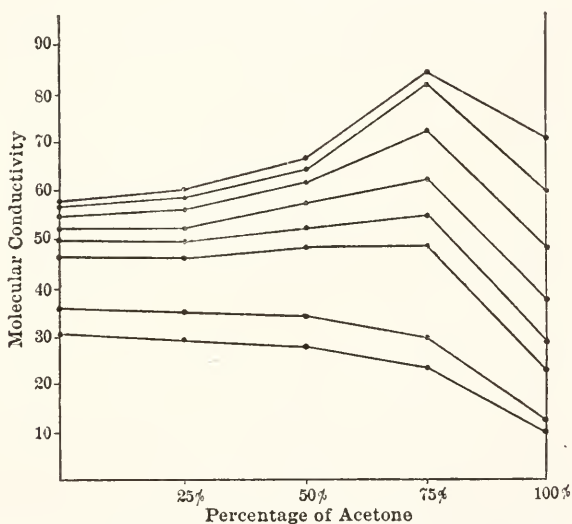


FIG. 58. — CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 0°.

#### COBALT CHLORIDE.

The cobalt chloride used in this work was obtained from Kahlbaum. No appreciable impurity could be detected. This salt can not be dehydrated in contact with the air, and special precautions must be taken to prevent the formation of the oxychloride. The salt containing 6 molecules of water was first placed over concentrated sulphuric acid, in a vacuum desiccator, for several days. It was thus deprived of part of its water of crystallization. It was then placed in an air-bath and dried at 140° to 150°, in a stream of dry hydrochloric acid gas. The salt was subsequently kept in a vacuum desiccator over sulphuric acid and potassium hydroxide. It gave no test for free hydrochloric acid, and possessed a pale, sky-blue color.

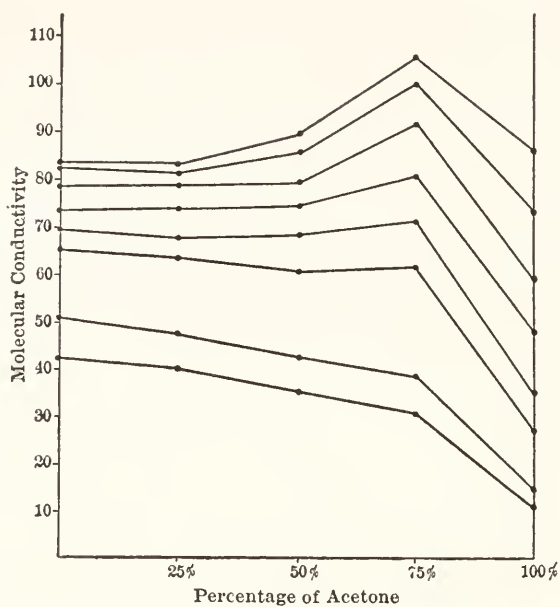


FIG. 59.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 25°.

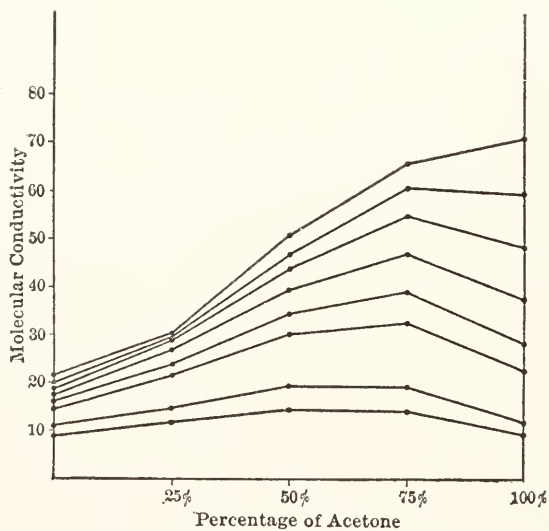


FIG. 60.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 0°.

Cobalt chloride, dissolved in methyl and ethyl alcohols and acetone, gives rise to a number of color phenomena. Spectroscopic observations concerning the color changes of cobalt chloride in water, methyl and ethyl alcohols, acetone, and binary mixtures of these solvents have been carried out in the physical chemical laboratory of the Johns Hopkins University by Jones and Uhler. The results of this work have been published by the Carnegie Institution of Washington.<sup>1</sup>

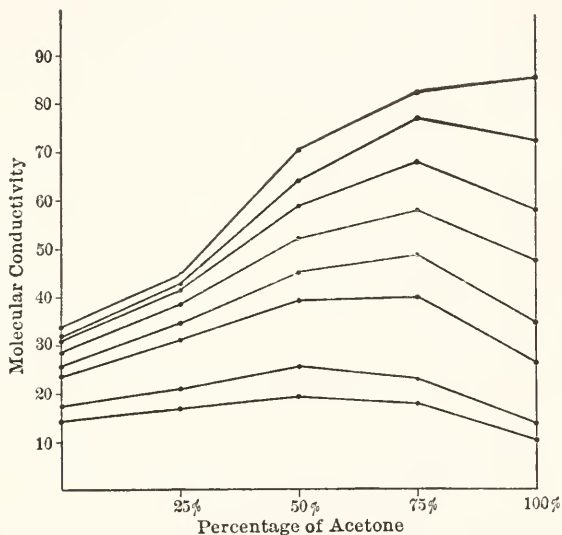


FIG. 61.—CONDUCTIVITY OF LITHIUM BROMIDE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 25°.

Hydrolysis probably comes into play, to some extent, in the more dilute aqueous solutions.

TABLE 71.—*Conductivity of cobalt chloride.*

$v$	In water at 0° and 25°.			In a mixture of 25 p. ct. methyl alcohol and water at 0° and 25°.			In a mixture of 50 p. ct. methyl alcohol and water at 0° and 25°.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	86.42	156.36	.0324	43.97	92.35	0.0440	32.94	65.85	0.0400
50	104.31	189.27	.0326	52.02	110.24	.0447	39.96	82.44	.0425
100	109.27	197.41	.0322	52.39	112.95	.0462	41.39	85.58	.0427
200	113.73	213.40	.0350	57.20	126.60	.0485	44.95	92.90	.0427
400	115.87	219.63	.0358	57.99	125.17	.0463	46.15	96.35	.0435
800	116.71	220.04	.0354	60.14	127.46	.0447	48.51	100.54	.0429
1600	117.40	221.50	.0355	61.98	133.98	.0472	51.40	104.19	.0411

<sup>1</sup> Publication No. 60, "Hydrates in Aqueous Solution."

TABLE 71.—*Conductivity of cobalt chloride.*—Continued.

$v$	In a mixture of 75 p. ct. methyl alcohol and water at 0° and 25°.			In methyl alcohol at 0° and 25°.			In a mixture of 25 p. ct. ethyl alcohol and water at 0° and 25°.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	27.40	49.58	0.0324	33.46	41.78	0.00995	30.53	73.68	0.0565
50	37.45	61.58	.0258	51.76	65.22	.01040	33.74	85.65	.0615
100	38.07	66.17	.0296	60.89	76.08	.00998	34.64	87.60	.0611
200	43.16	76.01	.0304	70.45	87.37	.00961	35.64	94.42	.0660
400	45.54	77.82	.0283	75.64	99.96	.01280	37.63	97.64	.0638
800	48.55	80.51	.0263	86.57	117.18	.01410	41.89	101.33	.0568
1600	51.39	84.39	.0257	95.54	133.33	.01580	42.42	103.86	.0579
$v$	In a mixture of 50 p. ct. ethyl alcohol and water at 0° and 25°.			In a mixture of 75 p. ct. ethyl alcohol and water at 0° and 25°.			In ethyl alcohol at 0° and 25°.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	18.17	44.75	0.0585	15.21	30.39	0.0399	6.06	7.64	0.0104
50	21.55	55.21	.0625	19.85	41.12	.0428	10.59	13.75	.0119
100	22.46	57.41	.0622	21.34	44.72	.0438	12.79	17.33	.0142
200	23.83	63.42	.0664	24.02	51.70	.0461	15.43	20.93	.0142
400	24.76	64.00	.0634	25.67	54.45	.0448	17.66	24.18	.0148
800	26.46	69.34	.0648	27.74	59.56	.0459	20.70	28.45	.0150
1600	28.68	70.51	.0583	29.61	63.87	.0463	23.99	33.59	.0160
$v$	In a mixture of 25 p. ct. methyl alcohol and ethyl alcohol at 0° and 25°.			In a mixture of 50 p. ct. methyl alcohol and ethyl alcohol at 0° and 25°.			In a mixture of 75 p. ct. methyl alcohol and ethyl alcohol at 0° and 25°.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	8.82	10.76	0.00880	12.89	16.89	0.0124	22.49	25.53	0.00541
50	14.66	17.61	.00805	21.46	27.38	.0110	35.33	44.31	.01020
100	17.32	21.75	.01022	24.31	30.39	.0100	40.79	49.90	.00893
200	20.23	26.58	.01255	28.63	35.89	.0101	48.55	60.62	.00994
400	23.75	30.08	.01070	32.28	41.80	.0118	54.78	69.42	.01070
800	28.34	35.23	.00972	39.21	48.22	.0092	63.06	81.13	.01150
1600	32.23	41.14	.01106	46.28	58.73	.0108	69.29	95.07	.01490
$v$	In a mixture of 25 p. ct. acetone and water at 0° and 25°.			In a mixture of 50 p. ct. acetone and water at 0° and 25°.					
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.			
100	64.40	115.38	0.0316	54.42	96.89	0.0312			
200	67.88	118.42	.0298	57.79	106.88	.0340			
400	69.13	122.39	.0308	60.29	112.70	.0348			
800	72.93	126.88	.0296	64.54	117.97	.0331			
1600	79.34	134.69	.0279	67.80	125.54	.0341			
$v$	In a mixture of 75 p. ct. acetone and water at 0° and 25°.			In acetone at 0° and 25°.					
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.			
100	33.14	70.57	0.0452	10.18	9.47	— 0.00279			
200	37.98	84.48	.0490	10.96	9.70	— .00460			
400	53.41	94.84	.0310	11.63	9.94	— .00581			
800	61.16	109.76	.0318	12.66	10.11	— .00806			
1600	68.51	124.95	.0329	12.79	10.45	— .00732			



TABLE 71. — *Conductivity of cobalt chloride.* — Continued.

$v$	In a mixture of 25 p. ct. acetone and methyl alcohol at 0° and 25°.			In a mixture of 50 p. ct. acetone and methyl alcohol at 0° and 25°.			In a mixture of 75 p. ct. acetone and methyl alcohol at 0° and 25°.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
100	48.10	56.28	0.00680	35.31	39.20	0.00441	23.85	24.83	+ 0.00164
200	57.33	64.87	.00526	42.12	46.94	.00458	28.72	28.67	— .00007
400	64.43	73.04	.00534	49.39	55.47	.00492	32.74	31.85	— .00108
800	74.60	84.46	.00529	56.97	66.85	.00694	42.05	38.69	— .00319
1600	91.57	100.09	.00372	67.55	74.11	.00388	50.94	47.20	— .00294

$v$	In a mixture of 25 p. ct. acetone and ethyl alcohol at 0° and 25°.			In a mixture of 50 p. ct. acetone and ethyl alcohol at 0° and 25°.			In a mixture of 75 p. ct. acetone and ethyl alcohol at 0° and 25°.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
100	14.40	15.43	0.00286	12.78	12.41	— 0.00116	13.46	11.95	— 0.00449
200	18.05	19.47	.00314	15.20	13.91	— .00339	14.41	12.49	— .00533
400	21.19	23.67	.00562	17.95	15.78	— .00483	14.69	12.69	— .00544
800	26.10	30.20	.00628	22.47	18.76	— .00660	15.74	13.48	— .00574
1600	31.80	36.41	.00580	28.67	23.47	— .00726	17.28	14.19	— .00715

TABLE 72. — *Comparison of the conductivities of cobalt chloride.*

$v$	In mixtures of methyl alcohol and water at 0°.					In mixtures of methyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	86.42	43.97	32.94	27.40	33.46	156.36	92.35	65.85	49.58	41.78
50	104.31	52.02	39.96	37.45	51.76	189.27	110.24	82.44	61.58	65.22
100	109.27	52.39	41.39	38.07	60.89	197.41	112.95	85.58	66.17	76.08
200	113.73	57.20	44.95	43.16	70.45	213.40	126.60	92.90	76.01	87.37
400	115.87	57.99	46.15	45.54	75.64	219.63	125.17	96.35	77.82	99.96
800	116.71	60.14	48.51	48.55	86.57	220.04	127.46	100.54	80.51	117.18
1600	117.40	61.98	51.40	51.39	95.54	221.50	133.98	104.19	84.39	133.33

$v$	In mixtures of ethyl alcohol and water at 0°.					In mixtures of ethyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	86.42	30.53	18.17	15.21	6.06	156.36	73.68	44.75	30.39	7.64
50	104.31	33.74	21.55	19.85	10.59	189.27	85.65	55.21	41.12	13.75
100	109.27	34.64	22.46	21.34	12.79	197.41	87.60	57.41	44.72	17.33
200	113.73	35.64	23.83	24.02	15.43	213.40	94.42	63.42	51.70	20.93
400	115.87	37.63	24.76	25.67	17.66	219.63	97.64	64.00	54.45	24.18
800	116.71	41.89	26.46	27.74	20.70	220.40	101.33	69.34	59.56	28.45
1600	117.40	42.42	28.68	29.61	23.99	221.50	103.86	70.51	63.87	33.59

$v$	In mixtures of methyl alcohol and ethyl alcohol at 0°.					In mixtures of methyl alcohol and ethyl alcohol at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	6.06	8.82	12.89	22.49	33.46	7.64	10.76	16.89	25.53	41.78
50	10.59	14.66	21.46	35.33	51.76	13.75	17.61	27.38	44.31	133.33
100	12.79	17.32	24.31	40.79	60.89	17.33	21.75	30.39	49.90	76.08
200	15.43	20.23	28.63	48.55	70.45	20.93	26.58	35.89	60.62	87.37
400	17.66	23.75	32.28	54.78	75.64	24.18	30.08	41.80	69.42	99.96
800	20.70	28.34	39.21	63.06	86.57	28.45	35.23	48.22	81.13	117.18
1600	23.99	32.23	46.28	69.29	95.54	33.59	41.14	58.73	95.07	133.33

TABLE 72. — Comparison of the conductivities of cobalt chloride. — Continued.

$\nu$	In mixtures of acetone and water at 0°.					In mixtures of acetone and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
100	109.27	64.40	54.42	33.14	10.18	197.41	115.38	96.89	70.57	9.47
200	113.73	67.88	57.79	37.98	10.96	213.40	118.42	106.88	84.48	9.70
400	115.87	69.13	60.29	53.41	11.63	219.63	122.39	112.70	94.84	9.94
800	116.71	72.93	64.54	61.16	12.66	220.04	126.88	117.97	109.76	10.11
1600	117.40	79.34	67.80	68.51	12.79	221.50	134.69	125.54	124.95	10.45
$\nu$	In mixtures of acetone and methyl alcohol at 0°.					In mixtures of acetone and methyl alcohol at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
100	60.89	48.10	35.31	23.85	10.18	76.08	56.28	39.20	24.83	9.47
200	70.45	57.33	42.12	28.72	10.96	87.37	64.87	46.94	28.67	9.70
400	75.64	64.43	49.39	32.74	11.63	99.96	73.04	55.47	31.85	9.94
800	86.57	74.60	56.97	42.05	12.66	117.18	84.46	66.85	38.69	10.11
1600	95.54	91.57	67.55	50.94	12.79	133.33	100.09	74.11	47.20	10.45
$\nu$	In mixtures of acetone and ethyl alcohol at 0°.					In mixtures of acetone and ethyl alcohol at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
100	12.79	14.40	12.78	13.46	10.18	17.33	15.43	12.41	11.95	9.47
200	15.43	18.05	15.20	14.41	10.96	20.93	19.47	13.91	12.49	9.70
400	17.66	21.19	17.95	14.69	11.63	24.18	23.67	15.78	12.69	9.94
800	20.70	26.10	22.47	15.74	12.66	28.45	30.20	18.76	13.48	10.11
1600	23.99	31.80	28.67	17.28	12.79	33.59	36.41	23.47	14.19	10.45

TABLE 73. — Comparison of the temperature coefficients of conductivity of cobalt chloride from 0° to 25°.

In mixtures of—	$\nu$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Methyl alcohol and water . . . . .	10	0.0324	0.0440	0.0400	0.0324	0.00995
	50	.0326	.0447	.0425	.0258	.01040
	100	.0322	.0462	.0427	.0296	.00998
	200	.0350	.0485	.0427	.0304	.00961
	400	.0358	.0463	.0435	.0283	.01280
	800	.0354	.0447	.0429	.0263	.01410
	1600	.0355	.0472	.0411	.0257	.01580
Ethyl alcohol and water . . . . .	10	0.0324	0.0565	0.0585	0.0399	0.0104
	50	.0326	.0615	.0625	.0428	.0119
	100	.0322	.0611	.0622	.0438	.0142
	200	.0350	.0660	.0664	.0461	.0142
	400	.0358	.0638	.0634	.0448	.0148
	800	.0354	.0568	.0648	.0459	.0150
	1600	.0355	.0579	.0583	.0463	.0160
Methyl alcohol and ethyl alcohol . .	10	0.0104	0.00880	0.0124	0.00541	0.00995
	50	.0119	.00805	.0110	.01020	.01040
	100	.0142	.01023	.0100	.00893	.00998
	200	.0142	.01255	.0101	.00994	.00961
	400	.0148	.01070	.0118	.01070	.01280
	800	.0150	.00972	.0092	.01150	.01410
	1600	.0160	.01106	.0108	.01490	.01580

TABLE 73.—Comparison of the temperature coefficients of conductivity of cobalt chloride from 0° to 25°.—Continued.

In mixtures of	$\nu$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	
Acetone and water .	10	.....	.....	.....	.....	.....	
	50	.....	.....	.....	.....	.....	
	100	0.0322	0.0316	0.0312	0.0452	-0.00279	
	200	.0350	.0298	.0340	.0490	-.00460	
	400	.0358	.0308	.0348	.0310	-.00581	
	800	.0354	.0296	.0331	.0318	-.00806	
	1600	.0355	.0279	.0341	.0329	-.00732	
Acetone and methyl alcohol . . . . .	100	0.00998	0.00680	0.00441	+0.00164	-0.00279	
	200	.00961	.00526	.00458	-.00007	-.00460	
	400	.01280	.00534	.00492	-.00108	-.00581	
	800	.01410	.00529	.00694	-.00319	-.00806	
		1600	.01580	.00372	.00388	-.00294	-.00732
	Acetone and ethyl alcohol . . . . .	100	0.0142	0.00286	-0.00116	-0.00449	-0.00279
200		.0142	.00314	-.00339	-.00533	-.00460	
400		.0148	.00562	-.00483	-.00544	-.00581	
800		.0150	.00628	-.00660	-.00574	-.00806	
		1600	.0160	.00580	-.00726	-.00715	-.00732

Tables 71 and 72 (figs. 62 and 63), for cobalt chloride in mixtures of methyl alcohol and water, show a minimum in conductivity at both tempera-

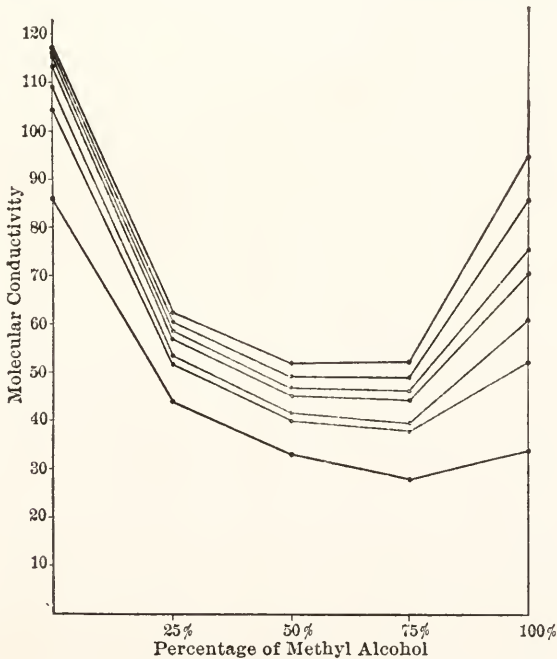


FIG. 62.—CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 0°.

tures. It should be noticed that the minimum, which occurs in the 75 per cent mixture at both temperatures, is more marked at 25° than at 0°. In the case of lithium bromide, in mixtures of methyl alcohol and water, the minimum appeared more pronounced at the lower temperature. Between the 75 per cent mixture and pure ethyl alcohol the curves diverge rapidly from each other. This seems to indicate that the dissociation is greatly increased by the addition of small amounts of water.

The temperature coefficients increase with the dilution, especially in the aqueous and pure methyl alcohol solutions. The temperature coefficients are greater in the mixtures than in the pure solvents, reaching a maximum in the 25 per cent mixture.

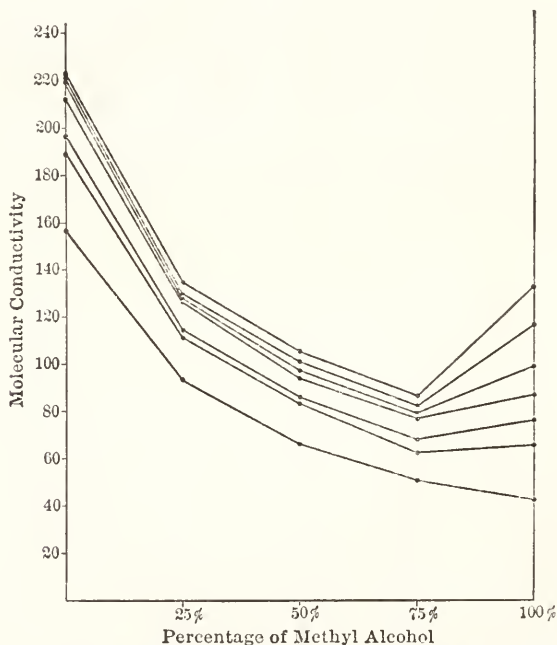


FIG. 63.—CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 25°.

Tables 71 and 72 (figs. 64 and 65), for cobalt chloride in mixtures of ethyl alcohol and water, show a point of inflection. At 0° the inflection of the curves exists at all dilutions, while at 25° the inflection is marked only at the high dilutions. Jones and Bingham obtained curves showing points of inflection while working with calcium nitrate, in mixtures of acetone and water.

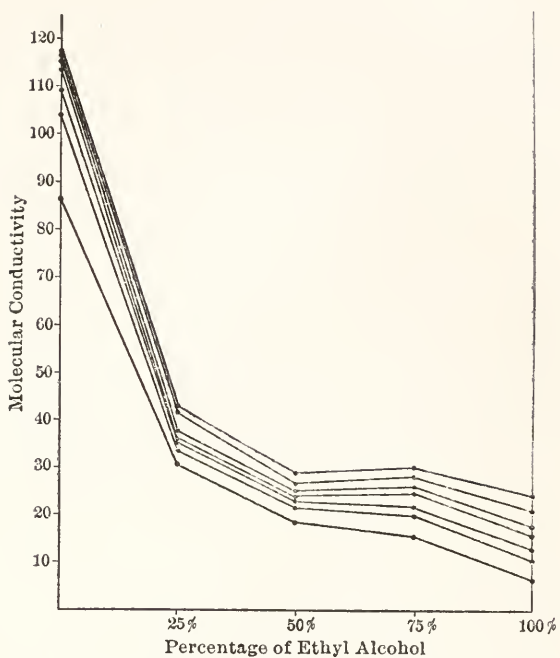


FIG. 64.—CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 0°.

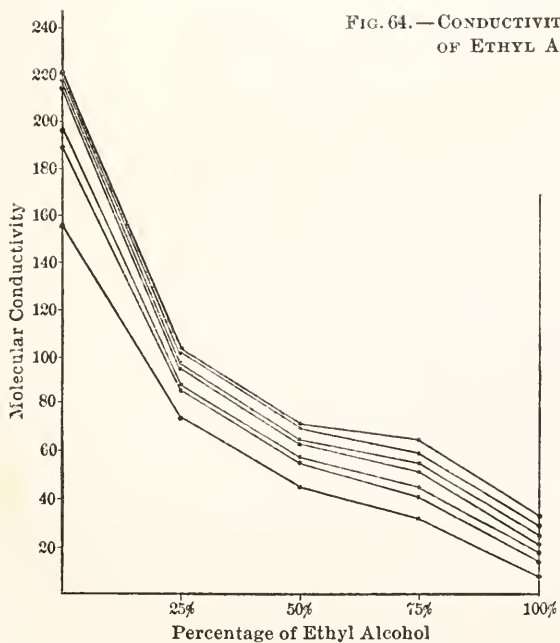


FIG. 65.—CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°.

In the pure ethyl alcohol the temperature coefficients increase with the dilution. They are largest, for the most part, in the 50 per cent mixture.

Tables 71 and 72 (figs. 66 and 67) make it clear that in a mixture of methyl and ethyl alcohols the conductivity of cobalt chloride exhibits no minimum value. There is a sagging of the curves, which demonstrates that the values obtained are less than what we should expect from the law of averages.

Tables 71 and 72 (figs. 68 and 69), for cobalt chloride in mixtures of acetone and water, show a point of inflection at low temperatures and high dilution. Attention should be called to the fact that the *conductivity values in pure acetone at 25° are less than the corresponding values at 0°, thus giving negative temperature coefficients*. The values in pure acetone for  $\mu_v$  are small at both temperatures and at all dilutions.

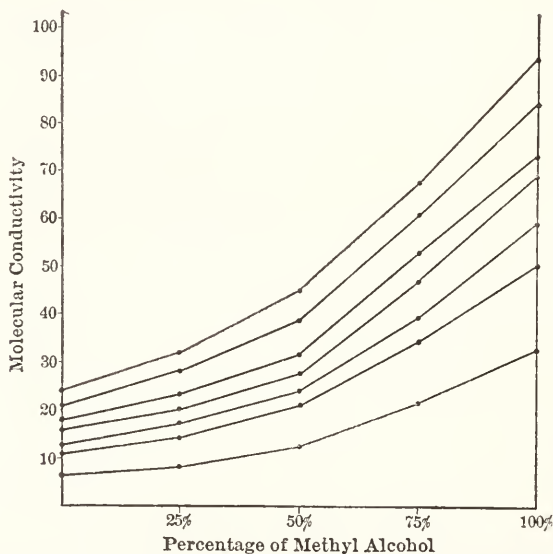


FIG. 66. — CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 0°.

From a study of tables 71 and 72 (figs. 70 and 71) we see that cobalt chloride, in mixtures of acetone and methyl alcohol, gives neither a minimum nor a maximum in conductivity. The values at most of the dilutions are what we should expect from the law of averages. It should be recalled that lithium bromide, in mixtures of acetone and methyl alcohol, gives a maximum in conductivity at both temperatures.

By studying the temperature coefficients we see that we have to deal with a peculiar phenomenon. In the pure acetone, as already stated, we have *negative temperature coefficients*. In the 75 per cent mixture of acetone and methyl alcohol, beginning with  $v = 400$ , we again have *negative temperature coefficients*. For  $v = 100$  we have the temperature coefficients *positive*, while at  $v = 200$  we have practically *no temperature coefficient of conductivity*.

Tables 71 and 72 (figs. 72 and 73), for cobalt chloride in mixtures of acetone and ethyl alcohol, give a maximum in conductivity in the 25 per cent mixture, especially at high dilutions.

In the mixtures of acetone and ethyl alcohol we have *negative temperature coefficients*, not only in the pure acetone and 75 per cent mixture, but also in the 50 per cent mixture. In the case of acetone and methyl alcohol, the temperature coefficients were *negative* only in the pure acetone and 75 per cent mixture. With increase of dilution we have an increase in value of the temperature coefficients, not only in the pure solvents, but also in the mixtures.

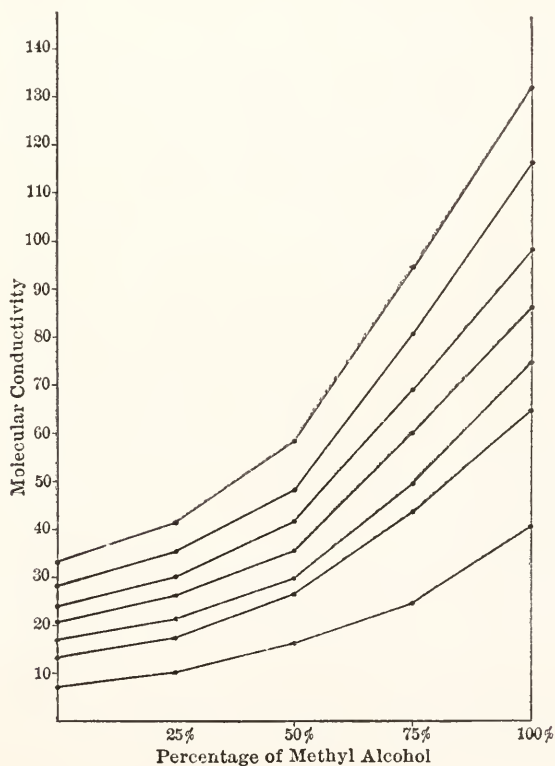


FIG. 67.—CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 25°.

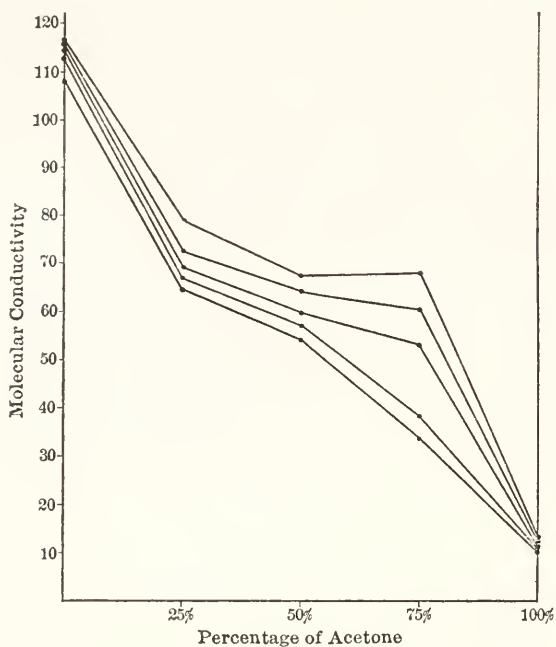


FIG. 68. — CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ACETONE AND WATER AT 0°.

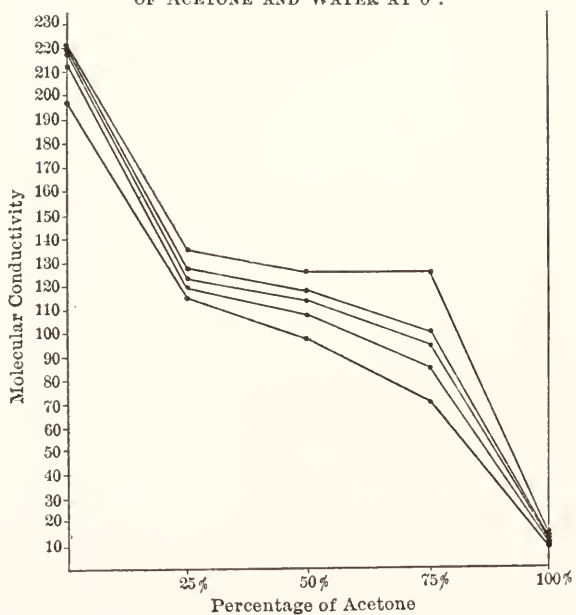


FIG. 69. — CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ACETONE AND WATER AT 25°.



## VISCOSITY MEASUREMENTS.

It can be shown that the rate  $\frac{dx}{dt}$ , at which the angular distortion of a portion of fluid changes, is proportional to the shearing stress upon the portion of the fluid. This ratio, shearing stress ( $S$ ) divided by  $\frac{dx}{dt}$ , for a given fluid, is called its coefficient of viscosity. It may be written thus,

$$\eta = \frac{S}{\frac{dx}{dt}}$$

in which  $\eta$  is the coefficient of viscosity.

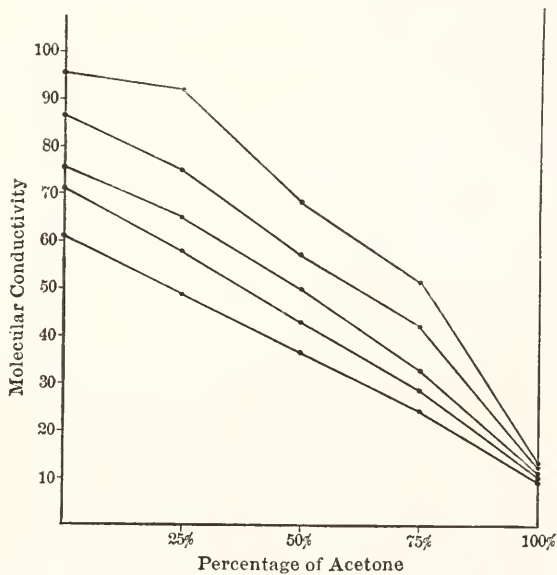


FIG. 70.—CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 0°.

The viscosity of fluids is often determined by the methods of Poiseuille and of Hagenbach. The viscosity is calculated by the formula <sup>1</sup>

$$\mu = \frac{P\pi r^4 t}{8vl}$$

where  $P$  is the actual pressure, diminished by that pressure which would be necessary to give to the fluid, while flowing through capillary tubes, the

<sup>1</sup> Hagenbach: Pogg. Ann., 19, 385 (1860).

kinetic energy possessed by it;  $t$  is the time of flow through the capillary tube of radius  $r$  and length  $l$ ;  $v$  is the volume of fluid flowing in time  $t$ .

The viscosity of fluids is, however, most commonly found by the method recommended by Ostwald.<sup>1</sup> We find by this method the time of flow of a fixed volume through a capillary tube, under the pressure due to the difference in level of the free surfaces of the fluid. The viscosity is found from the ratio of the time of flow for the fluid in question to the time of flow for an equal volume of water, multiplied by the specific gravity of the solution. This is expressed by the formula

$$\eta = \eta_0 \frac{St}{S_0 t_0}$$

in which  $\eta_0$  is the coefficient of viscosity for water,  $S_0$  its specific gravity, and

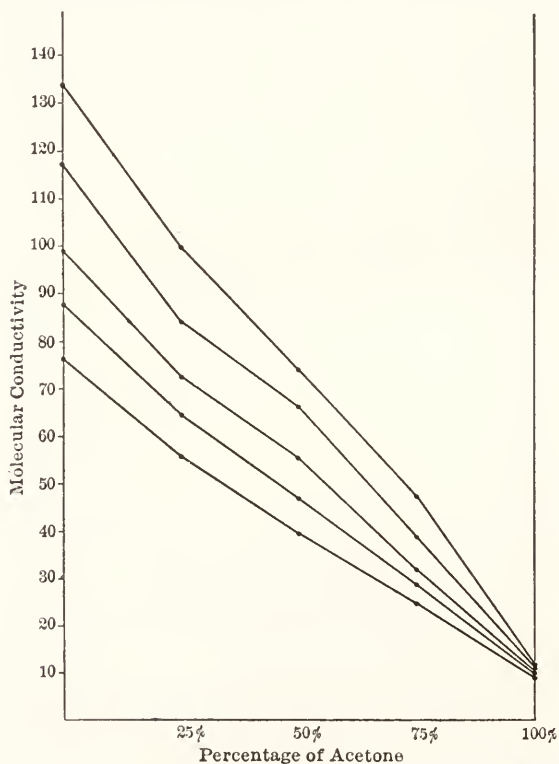


FIG. 71.—CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 25°.

$t_0$  its time of flow, at a given temperature. The specific gravity and time of flow of the liquid in question are given by  $S$  and  $t$ , respectively.

<sup>1</sup> Ostwald-Luther: Physiko-Chemische Messungen, Zweite Aufl., p. 259.

In tables 74 to 76, containing viscosity data, the values for pure water, at 0° and 25°, taken from the work of Thorpe and Rodger, are used, and all the other values are referred to them;  $\eta$  is the viscosity, while  $\phi$ , which represents fluidity, is obtained from the expression

$$\phi = \frac{1}{\eta}$$

The density of the liquid in question at 0° and 25° was compared with the density of water at 0° and 25°, respectively. The density of water at 0° and 25° was taken from data given in Landolt and Börnstein's tables.

The values of  $\eta$  and  $\phi$  for the solvents methyl alcohol, ethyl alcohol, acetone, and mixtures of these, are taken from the work of Jones and Bingham.

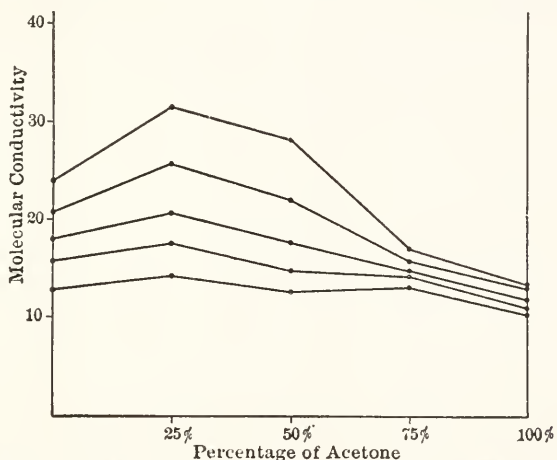


FIG. 72. — CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 0°.

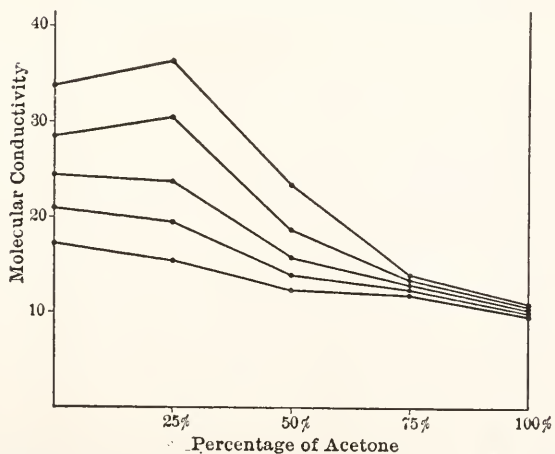


FIG. 73. — CONDUCTIVITY OF COBALT CHLORIDE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 25°.

TABLE 74. — *Fluidities.*

At 0 and 25°.	$\nu$	$\mu^0$	$\phi^0$	$\mu^{25}$	$\phi^{25}$	Temperature coefficient.
Water . . . . .	Solvent	0.01778	56.24	0.00891	112.3	0.0398
Lithium bromide in water .	10	.01874	53.36	.009077	110.17	.0425
	1600	.01827	54.73	.008963	111.57	.0415
LITHIUM BROMIDE IN						
Mixture of 25 p. ct. methyl alcohol and water . . .	Solvent	.01778	56.24	.008910	112.30	.0398
	10	.034216	29.22	.01440	69.43	.0550
	1600	.....	.....	.01420	70.42	.....
	Solvent	.03335	29.98	.01409	70.94	.0546
Mixture of 50 p. ct. methyl alcohol and water . . .	10	.03703	27.00	.01680	59.53	.0482
	1600	.....	.....	.01639	61.01	.....
	Solvent	.03642	27.46	.01611	62.04	.0503
	10	.....	.....	.01345	74.32	.....
Mixture of 75 p. ct. methyl alcohol and water . . .	1600	.....	.....	.01298	77.00	.....
	Solvent	.02576	38.32	.01283	77.92	.0402
Methyl alcohol . . . . .	10	.008994	111.18	.006124	163.28	.0187
	1600	.008346	119.82	.005635	177.46	.0192
	Solvent	.008185	122.20	.005659	176.70	.0178
	10	.....	.....	.01832	54.57	.....
Mixture of 25 p. ct. ethyl alcohol and water . . .	1600	.....	.....	.01818	55.00	.....
	Solvent	.05264	18.99	.01810	55.22	.0763
Mixture of 50 p. ct. ethyl alcohol and water . . .	10	.06922	14.45	.02453	40.77	.0728
	1600	.....	.....	.02407	41.53	.....
	Solvent	.06720	14.88	.02405	41.56	.0717
	10	.....	.....	.02204	45.36	.....
Mixture of 75 p. ct. ethyl alcohol and water . . .	1600	.....	.....	.02139	46.75	.....
	Solvent	.05167	19.35	.02118	47.21	.0575
Ethyl alcohol . . . . .	10	.02441	40.96	.01366	73.18	.0314
	1600	.02199	45.48	.01224	81.69	.0318
	Solvent	.01856	53.88	.01106	90.35	.0271
	10	.....	.....	.01366	73.19	.....
Mixture of 25 p. ct. acetone and water . . . . .	1600	.....	.....	.01356	73.72	.....
	Solvent	.0293	34.12	.01276	78.37	.0518
Mixture of 50 p. ct. acetone and water . . . . .	10	.03102	32.23	.01428	70.00	.0468
	1600	.....	.....	.01369	73.00	.....
	Solvent	.03027	33.03	.01330	74.96	.0508
	10	.....	.....	.009562	104.58	.....
Mixture of 75 p. ct. acetone and water . . . . .	1600	.....	.....	.009263	107.95	.....
	Solvent	.017	58.8	.008904	112.30	.0364
Acetone . . . . .	10	.004302	232.45	.003484	286.96	.0093
	1600	.004117	242.85	.003339	299.42	.0093
	Solvent	.004097	244.10	.003237	308.90	.0106
	10	.....	.....	.005455	183.30	.....
Mixture of 25 p. ct. acetone and methyl alcohol . . .	1600	.....	.....	.005068	197.29	.....
	Solvent	.006498	153.90	.004615	216.70	.0163
Mixture of 50 p. ct. acetone and methyl alcohol . . .	10	.006265	159.6 (?)	.004527	220.87	.0153
	1600	.005774	173.17	.004234	236.18	.0145
	Solvent	.005336	187.40	.003891	257.10	.0148
	10	.....	.....	.003775	264.88	.....
Mixture of 75 p. ct. acetone and methyl alcohol . . .	1600	.....	.....	.003581	279.25	.....
	Solvent	.004501	222.20	.003446	290.10	.0122
Mixture of 25 p. ct. acetone and ethyl alcohol . . .	10	.....	.....	.008218	121.69	.....
	1600	.....	.....	.007731	129.34	.....
	Solvent	.01041	96.08	.006714	148.90	.022
	10	.007353	136.0	.005554	180.05	.0129
Mixture of 50 p. ct. acetone and ethyl alcohol . . .	1600	.....	.....	.005165	193.59	.....
	Solvent	.006801	147.0	.004874	205.20	.0148
Mixture of 75 p. ct. acetone and ethyl alcohol . . .	10	.....	.....	.004237	235.99	.....
	1600	.....	.....	.003874	258.10	.....
	Solvent	.00499	200.4	.003776	264.80	.01296

TABLE 75. — Comparison of fluidities of lithium bromide at 0° and 25°.

Mixtures of—	At 0°.					
	$v$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Methyl alcohol and water . .	10	53.36	29.22	27.00	....	111.18
	1600	54.73	....	....	....	119.82
	Solvent	56.24	29.98	27.46	38.82	122.20
Ethyl alcohol and water . . .	10	53.36	....	14.45	....	40.96
	1600	54.73	....	....	....	45.48
	Solvent	56.24	18.99	14.88	19.35	53.88
Acetone and water . . . . .	10	53.36	....	32.23	....	232.45
	1600	54.73	....	....	....	242.85
	Solvent	56.24	34.12	33.03	58.80	244.10
Acetone and methyl alcohol . .	10	111.18	....	159.6(?)	....	232.45
	1600	119.82	....	173.17	....	242.85
	Solvent	122.20	153.90	187.40	222.20	244.10
Acetone and ethyl alcohol . .	10	40.96	....	136.00	....	232.45
	1600	45.48	....	....	....	242.85
	Solvent	53.88	96.08	147.00	200.40	244.10
Mixtures of—	At 25°.					
Methyl alcohol and water . . .	10	110.17	69.43	59.53	74.32	163.28
	1600	111.57	70.42	61.01	77.00	177.46
	Solvent	112.30	70.94	62.04	77.92	176.70
Ethyl alcohol and water . . .	10	110.17	54.57	40.77	45.36	73.18
	1600	111.57	55.00	41.53	46.75	81.69
	Solvent	112.30	55.22	41.56	47.21	90.35
Acetone and water . . . . .	10	110.17	73.19	70.00	104.58	286.96
	1600	111.57	73.72	73.00	107.95	299.42
	Solvent	112.30	78.37	74.96	112.30	308.90
Acetone and methyl alcohol . .	10	163.28	183.30	220.87	264.88	286.96
	1600	177.46	197.29	236.18	279.25	299.42
	Solvent	176.70	216.70	257.00	290.10	308.90
Acetone and ethyl alcohol . . .	10	73.18	121.69	180.05	235.99	286.96
	1600	81.69	129.34	193.59	258.10	299.42
	Solvent	90.35	148.90	205.20	264.80	308.90

TABLE 76. — Comparison of the temperature coefficients of lithium bromide from 0° to 25°.

Mixtures of—	$v$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Ethyl alcohol and water . . .	10	0.0425	....	0.0728	....	0.0314
	1600	.0415	....	....	....	.0318
	Solvent	.0398	0.0763	.0717	.00575	.0271
Methyl alcohol and water . . .	10	.0425	.0550	.0482	....	.0187
	1600	.0415	....	....	....	.0192
	Solvent	.0398	.0546	.0503	.0402	.0178
Acetone and water . . . . .	10	.0425	....	.0468	....	.0093
	1600	.0415	....	....	....	.0093
	Solvent	.0398	.0518	.0508	.0364	.0106
Acetone and methyl alcohol . .	10	.0187	....	.0153	....	.0093
	1600	.0192	....	.0145	....	.0093
	Solvent	.0178	.0163	.0148	.0122	.0106
Acetone and ethyl alcohol . . .	10	.0314	....	.0129	....	.0093
	1600	.0318	....	....	....	.0093
	Solvent	.0271	.022	.0148	.01296	.0106

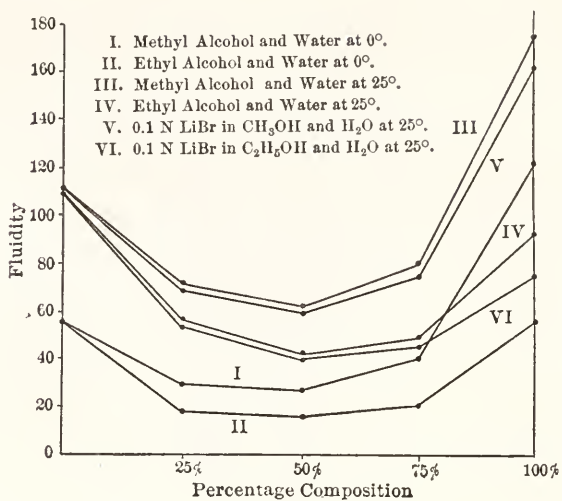


FIG. 74.

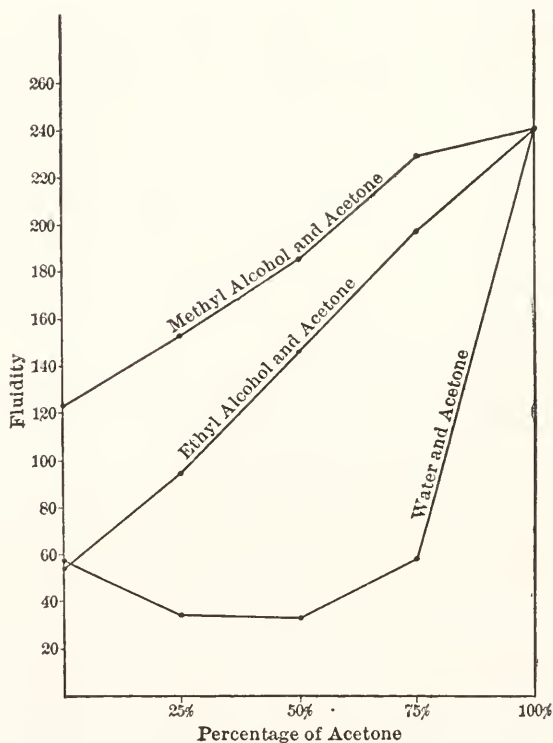


FIG. 75. — FLUIDITY OF SOLVENT MIXTURES AT 0°.

Tables 74 and 75 (fig. 74) show that there is a minimum of fluidity not only in the case of the mixtures of the pure solvents — methyl alcohol and water and ethyl alcohol and water — at both temperatures, but also in the case of lithium bromide dissolved in the above solvents. The fluidity of a liquid being the reciprocal of its viscosity, the viscosity curve would pass through a maximum in the above cases. A large number of investigations have been carried out on the viscosities of the alcohols and water, notably

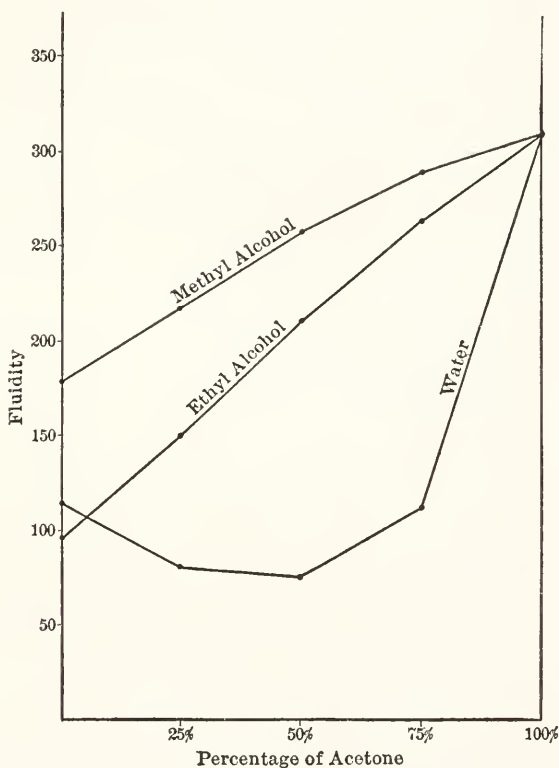


FIG. 76.—FLUIDITY OF SOLVENT MIXTURES AT 25°.

by Poisseuille,<sup>1</sup> Stephan,<sup>2</sup> Pagliani and Battelli,<sup>3</sup> Noack,<sup>4</sup> and Traube.<sup>5</sup> Quite recently some work has been done on the viscosity of mixtures of the alcohols and water by Dunstan,<sup>6</sup> Blanchard,<sup>7</sup> and Varenne and Godefroy.<sup>8</sup> All of these

<sup>1</sup> Mem. Inst. Paris, **9**, 433 (1896).

<sup>2</sup> Wied. Ann., **17**, 673 (1883).

<sup>3</sup> Atti. di R. Ac. delle Sc. d. Torino, **20**, 607 (1885).

<sup>4</sup> Wied. Ann., **27**, 289 (1886).

<sup>5</sup> Ber. d. chem. Gesell., **19**, 871 (1886).

<sup>6</sup> Journ. Chem. Soc., **85**, 817 (1904).

<sup>7</sup> Journ. Amer. Chem. Soc., **26**, 1315 (1904).

<sup>8</sup> Compt. rend., **137**, 992 (1903); **138**, 990 (1904).

workers have found that, in the case of mixtures of the alcohols and water, the viscosity of the mixture is much greater than would be expected from the law of averages.

Jones and Carroll<sup>1</sup> have calculated the various fluidities of mixtures of methyl and ethyl alcohols and water, for the temperatures 0°, 10°, 20°, and 30°, from the results of Pagliani and Battelli<sup>1</sup> and of Traube,<sup>1</sup> and have plotted the fluidity curves. Their curves were similar to those which we obtained.

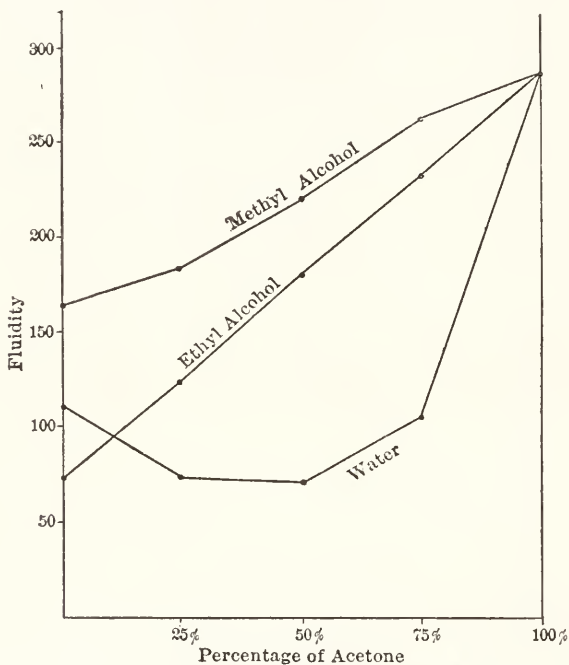


FIG. 77. — N/10 LITHIUM BROMIDE IN ACETONE MIXTURES AT 25°.

Tables 74 and 75 (figs. 75, 76, and 77) show that there is a minimum of fluidity for the solvents only in the case of acetone and water. This fact was pointed out by Jones and Bingham. Lithium bromide, in a mixture of acetone and water, shows a similar minimum. Jones and Bingham also found that in the mixtures of acetone with methyl alcohol somewhat larger values were obtained than would be expected from the fluidities of the pure solvents. This effect is not quite so apparent in the case of acetone and ethyl alcohol. We obtained similar results in the case of lithium bromide in these solvents. It is to be especially noticed that the viscosity curves in all cases, for mixtures of acetone with the alcohols, show a marked sagging.

<sup>1</sup> Loc. cit.



TABLE 77. — Comparison of the temperature coefficients of conductivity and fluidity.

Mixtures of—		$v$	Dis- solved sub- stance.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Methyl alcohol and water.	Fluidity . .	Solvent	....	0.0398	0.0456	0.0503	0.0402	0.0178
		10	LiBr	.0329	.0435	.0410	.0314	.01590
	Conductivity	1600	LiBr	.0357	.0437	.0420	.0335	.01810
		10	CoCl <sub>2</sub>	.0324	.0440	.0400	.0324	.00995
		1600	CoCl <sub>2</sub>	.0355	.0472	.0411	.0257	.01580
Ethyl alcohol and water.	Fluidity . .	Solvent	....	.0398	.0763	.0717	.0575	.0271
		10	LiBr	.0329	.0557	.0595	.0437	.0253
	Conductivity	1600	LiBr	.0357	.0448	.0596	.0465	.0242
		10	CoCl <sub>2</sub>	.0324	.0565	.0585	.0399	.0104
		1600	CoCl <sub>2</sub>	.0355	.0579	.0583	.0463	.0100
Acetone and water.	Fluidity . .	Solvent	....	.0398	.0518	.0508	.0364	.0106
		10	LiBr	.0329	.0429	.0432	.0315	.00729
	Conductivity	1600	LiBr	.0357	.0401	.0437	.0372	.00847
		100	CoCl <sub>2</sub>	.0322	.0316	.0312	.0452	.00279
		1600	CoCl <sub>2</sub>	.0355	.0279	.0341	.0329	.00732
Acetone and methyl alcohol.	Fluidity . .	Solvent	....	.0178	.0163	.0148	.0122	.0106
		10	LiBr	.0159	.0143	.00939	.0112	.00729
	Conductivity	1600	LiBr	.0181	.0153	.01340	.0104	.00847
		100	CoCl <sub>2</sub>	.00998	.0068	.00441	.00164	.00279
		1600	CoCl <sub>2</sub>	.0159	.00372	.00388	.00294	.00732
Acetone and ethyl alcohol.	Fluidity . .	Solvent	....	.0271	.022	.0148	.0129	.0106
		10	LiBr	.0253	.0168	.0135	.0085	.00729
	Conductivity	1600	LiBr	.0242	.0206	.0159	.0103	.00847
		100	CoCl <sub>2</sub>	.0142	.00286	.00116	.00449	.00279
		1600	CoCl <sub>2</sub>	.0160	.00580	.00726	.00715	.00732

Table 77 shows that the temperature coefficients of fluidity and conductivity, in the case of lithium bromide, vary in the same manner, although the latter are, for the most part, smaller than the former. Abnormal results were obtained with cobalt chloride in mixtures of acetone with the alcohols, in so far as the temperature coefficients of conductivity are concerned.

## DISCUSSION OF RESULTS.

## FLUIDITY AND CONDUCTIVITY.

That there is a parallelism between conductivity and fluidity has been previously pointed out in the introduction to this section; and since the conductivity of a solution is dependent, in part, upon its fluidity, we shall first discuss the fluidity curves and then, in connection with them, the conductivity curves.

When methyl alcohol, ethyl alcohol, or acetone is mixed with water, there is a contraction in volume and an evolution of heat, and we have a large deviation of the fluidity curve from a straight line. In other words, we have a marked viscosity maximum — a fact which frequently manifests itself when water and organic solvents are mixed. In addition to methyl and ethyl alcohols and acetone, propyl and isopropyl alcohols, propionic acid, butyric

and isobutyric acids, when mixed with water, show viscosity maxima. In every case there is a greater decrease in fluidity than would be expected from the law of averages.

When methyl and ethyl alcohols are mixed, they do not exhibit the same phenomena as is shown in the case of mixtures of organic solvents with water. Arrhenius<sup>1</sup> states that there is no observable change when these alcohols are brought together.

When acetone is mixed with methyl or ethyl alcohol, the fluidity curve of the mixture is approximately a straight line. The same is true when we have an electrolyte dissolved in mixtures of these solvents.

From a consideration of the fluidity curves and conductivity curves for lithium bromide in mixtures of methyl alcohol and water, it is quite evident that the minimum of fluidity corresponds to the minimum of conductivity, both generally occurring in the 50 per cent mixtures of the solvents. The drop in fluidity is more pronounced at the lower temperature, and, similarly, the drop in conductivity. In fact, at the higher temperature the minimum of conductivity occurs in the 75 per cent mixture until  $v = 100$ , where there is a shifting of the minimum to the 50 per cent mixture.

In the case of mixtures of ethyl alcohol and water, the minimum of fluidity is in the 50 per cent mixture, and more marked at the lower temperature. The conductivity minimum in this case occurs in the 75 per cent mixture, and is very slight indeed at 25°, although the values in each case are much less than we should expect from the law of averages. Thus, we have in both the case of methyl alcohol and water and of ethyl alcohol and water, a tendency for the shifting of the minimum towards the mixture containing the greater per cent of alcohol, whenever we have a rise in temperature.

Stephan,<sup>2</sup> working with mixtures of ethyl alcohol and water, found that the temperature coefficients of conductivity and of fluidity were very similar. A minimum in his curves was observed, and he proposed the relations—

$$k = \frac{KH}{\eta} \quad \text{and} \quad k = \frac{wKH}{w'\eta}$$

the first holding for the mixtures up to the minimum point, and the second from that point on.  $K$  is the same in both formulæ, and is the conductivity of the equivalent aqueous solution of the electrolyte;  $k$  is the conductivity in the mixture;  $H$  and  $\eta$  are the viscosity coefficients for water and for the mixture, respectively.  $w$  and  $w'$  are the per cents of water in the mixture and in the aqueous alcoholic mixtures of minimal fluidity, respectively. Stephan concluded that each ion carries with it molecules of the solvent, and that the ionic friction consists in friction between these molecules and the rest of the solvent. Thus we have very early the idea of ionic hydration introduced.

<sup>1</sup> Ztschr. phys. Chem., 1, 285 (1887).

<sup>2</sup> Wied. Ann., 17, 673 (1882).

This idea of ionic hydration, or ionic spheres, was further extended by Kohlrausch,<sup>1</sup> who proposed the hypothesis that—

About every ion there moves an atmosphere of the solvent, the dimensions of which are determined by the individual characteristics of the ion. . . . The electrolytic resistance is a frictional one that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portions of the solvent diminishes as the atmosphere becomes of greater dimensions. For a slow-moving ion there would be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, providing the atmosphere does not change its dimensions with temperature. However, if the atmosphere becomes smaller with rise in temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. This seems to be true for the slowest-moving, univalent ion, Li.

It will be recognized that this is essentially the theory of hydrates proposed by Jones.

In the case of the alcohols and water, this minimum of conductivity is entirely accounted for by some investigators on the basis of the formation of hydrates. This view was suggested by Zelinsky and Krapiwini.<sup>2</sup> The minimum in fluidity is attributed to the formation of molecular aggregations, which are formed by mixing the solvents. In the case of methyl alcohol and acetone, or ethyl alcohol and acetone, since the fluidity curve is a straight line, we conclude that the molecular aggregations of these solvents are not changed in size when the solvents are mixed. This is what we should expect if the fluidities are additive, a fact which has been shown recently by Bingham<sup>3</sup> to be true. From the above, we see that the conductivity minimum is generally accompanied by a fluidity minimum, and that both minima are more marked at the lower temperatures. Also, that an increase in temperature tends to shift the minimum towards the mixture containing a greater per cent of alcohol or acetone, as the case may be. Thus, we believe that *a diminution in the fluidity of the solvent, which would bring about a corresponding decrease in ionic mobility, is an important factor in causing the minimum of conductivity.* In the case when the conductivity minimum is in the 75 per cent mixture, while the minimum of fluidity is in the 50 per cent mixture, as it is with ethyl alcohol and water, we believe that the explanation is to be found in the fact that the ethyl alcohol and water mixtures have a much greater viscosity than those of methyl alcohol and water. When the minimum shifts with an increase in dilution, there may be an increase in dissociation.

However, we do not believe that the above explanation accounts entirely for the conductivity minimum. Since conductivity is dependent upon the number and velocity of the ions, there is no doubt that an increase in

<sup>1</sup> Proc. Roy. Soc., **71**, 338 (1903).  
Ztschr. phys. Chem., **21**, 35 (1896).

<sup>3</sup> Amer. Chem. Journ., **35**, 195 (1906).



where  $\eta_1$  and  $\eta_2$  are the viscosities of the components and  $H$  that of the mixture

$$K'_1 = K_1 + \frac{\eta_1}{\eta_2 - \eta_1}$$

where  $K_1$  has the same significance as in equation (1).

Since  $\frac{\eta_1\eta_2}{\eta_2 - \eta_1}$  is a constant, equation (2) is considered to represent an equilateral hyperbola, the  $Y$ -axis of which is at a distance  $\frac{\eta_1}{\eta_2 - \eta_1}$  to the left of the origin to which equation (1) is referred. Thus, the conclusion is drawn that the *hyperbola is the normal curve for viscosities and not the straight line*. This fact accounts for the sagging of the viscosity curves, or, in other words, the viscosities of the mixtures are not proportional directly to the amounts of the components. The above only holds in case we have a mixture of two liquids which are made up of particles that do not interact in any way with each other, as in the case of acetone and ethyl alcohol.

When we have contraction or expansion on mixing two liquids, the hyperbola would not represent the viscosity curve of the mixtures, but we get a curve of the form already described.

By examining the viscosity data of the mixtures of acetone with methyl alcohol and ethyl alcohol, and also the data for lithium bromide in these mixtures, we see that the viscosity of a mixture is, in most instances, slightly lower than would be expected from the law of averages. In these cases the fluidity curves are straight lines. In the recent work of Bingham this has been shown to be frequently true where organic solvents are mixed.

Let us now consider the maximum in conductivity obtained with lithium bromide in mixtures of acetone with methyl and ethyl alcohols. Cobalt chloride gave a maximum in conductivity only in the case of acetone with ethyl alcohol. In the former case the maximum occurs entirely in the 75 per cent mixture, while in the latter only in the 25 per cent mixture.

This phenomenon had also been observed by Jones and Bingham, working with lithium nitrate and calcium nitrate in mixtures of acetone with the alcohols. As pointed out by them, this must be due either to an increase in dissociation in the 75 per cent mixture, or to the diminution in the size of the ionic spheres.

In discussing the fluidity curves, we pointed out that when acetone was mixed with the alcohols, we did not obtain complex molecular aggregates. It is, then, impossible for the mixture to be more associated than the pure solvents, and we therefore can not have an increase in dissociation if the hypothesis of Dutoit and Aston is true.

From an examination of the conductivity tables of lithium bromide we see that we have by no means reached the limiting conductivity values in the

pure acetone, or the 75 per cent mixtures of acetone with the alcohols. It is nearly reached only with the pure alcohols. Thus we could not have complete dissociation in these mixtures. The conductivity maximum should also manifest itself in the case of cobalt chloride in mixtures of acetone with methyl alcohol, but this is contrary to what we have observed. We therefore accept the view, held tentatively by Jones and Bingham, that *the maximum in conductivity is due primarily to a change in the dimensions of the ionic spheres.*

Attention should be called to the fact that cobalt chloride, in mixtures of acetone with water, shows a tendency towards a maximum in conductivity in the 75 per cent mixture, notwithstanding the great decrease in fluidity.

Thus we see that the tendency towards a maximum in conductivity, in mixtures of acetone with other solvents, is very marked.

Let us now sum up the cases where maxima in conductivity have been obtained in the acetone mixtures. Jones and Bingham obtained the maximum with lithium nitrate and calcium nitrate in mixtures of acetone with methyl or ethyl alcohols. Under similar conditions, we have obtained the maximum in the case of lithium bromide in these mixtures. Cobalt chloride gave the maximum only in a mixture of acetone with ethyl alcohol.

Jones and Bingham showed that lithium nitrate and calcium nitrate, in mixtures of acetone with water, show a tendency towards a maximum. We have observed the same fact with cobalt chloride in a mixture of acetone with water.

#### TEMPERATURE COEFFICIENTS.

That conductivity is affected by temperature was observed as early as 1844 by Ohm.<sup>1</sup> In 1875 it was established by Kohlrausch<sup>2</sup> that the conductivity of aqueous solutions of electrolytes, in general, increases with the temperature, and that, for ordinary temperatures, this relation may be represented by the equation,

$$\lambda_t = \lambda_0 (1 + \alpha t)$$

where  $\lambda$  represents the molecular conductivity,  $t$  the temperature in question, and  $\alpha$  is a constant.

Arrhenius,<sup>3</sup> in 1889, showed, from theoretical considerations, that the relation between conductivity and temperature is not a linear one. He established the fact that conductivity at first increases with rise in temperature, reaches a maximum value, and then decreases. He verified this for solutions of hypophosphorous acid and phosphoric acid, the former having a maximum conductivity at about 55° and the latter at 75°.

<sup>1</sup> Pogg. Ann., **63**, 403 (1844).

<sup>2</sup> Ibid., **154**, 224 (1875).

<sup>3</sup> Ztschr. phys. Chem., **4**, 96 (1889).

Since Arrhenius made these measurements, maxima in conductivity have been found for solutions of copper sulphate and for a number of organic acids. The maximum conductivity of most aqueous solutions, however, is at so high a temperature that experimental difficulties have prevented the verification of the above theory of Arrhenius for many electrolytes.

Maxima of conductivity have been found by Miss Maltby,<sup>1</sup> Hagenbach,<sup>2</sup> Noyes and Coolidge,<sup>3</sup> and others, all working at high temperatures.

In the case of non-aqueous solvents there is more evidence available for the existence of conductivity-temperature curves, containing maxima.

Franklin and Kraus<sup>4</sup> found that, at high temperatures, the conductivity of solutions in liquid ammonia decreases with rise in temperature. Miss Maltby<sup>5</sup> showed that, at ordinary temperatures, the conductivity of an ethereal solution of hydrochloric acid decreases as the temperature rises. Cataneo<sup>6</sup> obtained negative temperature coefficients in ether and alcohol.

Kraus,<sup>7</sup> in his investigations of solutions in methyl and ethyl alcohols, also found that the conductivity passes through a maximum with rise in temperature.

Jones<sup>8</sup> explains these maxima in the conductivity curves thus:

The ions move faster and faster with rise in temperature, increasing the conductivity. The association of the solvent becomes less and less with rise in temperature and, consequently, its dissociating power becomes less and less. This, of course, diminishes the conductivity. The maximum in the conductivity curve represents the temperature at which *these opposite influences become equal*.

In a very recent article, Jones and West<sup>9</sup> have pointed out the effect of temperature on dissociation, and have worked out a large number of temperature coefficients of conductivity in aqueous solutions. They employed 32 substances, inorganic and organic, with very different degrees of dissociation. The range of temperature over which their investigation extended was from 0° to 35°. They found that, while conductivity increases with rise in temperature, dissociation decreases with rise in temperature.

Jones<sup>10</sup> has recently pointed out the bearing of hydrates on the temperature coefficients of conductivity of aqueous solutions. Jones and West, in their work, showed that with rise in temperature there was a decrease in dissociation. Therefore, *the increase in conductivity with rise in temperature is primarily due to an increase in the velocities with which the ions move*. The velocity of the ions is conditioned chiefly by the viscosity of the medium and the size

<sup>1</sup> Ztschr. phys. Chem., **18**, 155 (1895).

<sup>2</sup> Ann. d. Phys., **5**, 276 (1901).

<sup>3</sup> Ztschr. phys. Chem., **46**, 323 (1904).

Journ. Amer. Chem. Soc., **26**, 134 (1904).

<sup>4</sup> Amer. Chem. Journ., **24**, 83 (1900).

<sup>5</sup> Ztschr. phys. Chem., **18**, 133 (1895).

<sup>6</sup> Rend. Lincei [5], **2**, 1, 295 (1893); [5],  
**2**, 2, 112 (1893).

<sup>7</sup> Phys. Rev., **18**, 40 (1904).

<sup>8</sup> Amer. Chem. Journ., **31**, 584 (1904).

<sup>9</sup> Ibid., **34**, 357 (1905).

<sup>10</sup> Amer. Chem. Journ., **35**, 445 (1906).

of the ions. At the higher temperature the force which drives the ion is greater, and the fluidity of the medium through which the ion moves would be greater. Both of these factors increase the velocity of the ions and, consequently, increase the conductivity as the temperature is raised. Jones calls attention to the fact that the *mass of the ion decreases with rise in temperature*. He does not refer to the charged atom or group of atoms which are usually termed the ion, but to this charged nucleus plus a larger or smaller number of molecules of water, which are attached to it and which it drags along with it in its motion through the remainder of the solvent.

At the higher temperature the hydrate formed by the ion is less complex than at a lower temperature. The less the number of molecules of water combined with the ion, the smaller the mass of the ion and the less its resistance when moving through the solvent. Therefore, the ion will move faster at the higher temperature, and the conductivity of the solution will increase with rise in temperature.

Jones also points out the fact that, at the higher dilutions, the temperature coefficient of conductivity for any given substance is greater than at the lower dilutions. The hydrate at the higher dilution is more complex than at the lower. This being so, the change in the composition of the hydrate with change in temperature would be greater at the higher dilution and, consequently, the temperature coefficient of conductivity is greater the more dilute the solution.

After this brief review of the most important facts which have been found concerning the effect of temperature on conductivity, let us study the temperature coefficients which we obtained.

In a previous paper<sup>1</sup> we have pointed out the presence of *solvates* in non-aqueous solutions, not only in the case of lithium bromide, but also for several other electrolytes. That there is a combination of the solvent with the dissolved substance to form *solvates* is now a generally accepted fact.

In the pure solvents, with but one exception, the temperature coefficients of conductivity are greater at the higher dilutions than at the lower. This may be explained by the fact that if the solvate at the higher dilution is more complex than at the lower, then the change in the composition of the solvate in question, with change in temperature, is greater at the higher dilution. Consequently, the more dilute the solution the larger the temperature coefficient of conductivity.

In the mixtures of the solvents we found that, in practically every case, there was an increase in the temperature coefficients with increase in dilution. There is combination of the solvent and dissolved substance to form a *solvate*, and we believe the explanation is the same as that given above.

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<sup>1</sup> Amer. Chem. Journ., **35**, 316 (1906).



This same fact has been found to be true by Jones and his co-workers in many other cases. If we examine the data obtained by Jones and Lindsay in their work, we see that the temperature coefficients of conductivity increase with the dilution for potassium iodide, ammonium bromide, strontium iodide, and lithium nitrate, in mixtures of water, methyl and ethyl alcohols, and binary mixtures of these solvents. In some few cases the increase, however, is small. Similar results are found by a study of the work of Jones and Carroll, who worked with a number of electrolytes in mixtures of the same solvents. Jones and Bingham, in their work, observed the fact that in acetone, and in some few acetone mixtures, the temperature coefficients decreased with the dilution. In most cases, however, there was a slight increase with an increase in dilution.

Thus, the fact that at the higher dilutions the temperature coefficients are greater than at the lower, holds, in general, not only for aqueous solutions, as was pointed out by Jones, but also for organic solvents and for mixtures of these solvents in most of the cases thus far studied.

We have seen in the historical review that there are a few cases on record where the conductivity decreases with rise in temperature. This has been found to be true, generally, only at high temperatures and after a maximum had been reached. Bousfield and Lowry<sup>1</sup> have shown that we should expect this upper limit of conductivity on account of the decrease in dissociation with rise in temperature. They combine the formula of Slotte<sup>2</sup> for variation of fluidity—

$$\frac{\eta_0}{\eta} = l + \beta t)^n$$

which holds at low temperatures, with that of Abegg and Seitz for decrease in dielectric constant,

$$\frac{D}{D'} = e^{-at}$$

and give as the complete formula, which represents the effect of temperature on conductivity,

$$\frac{K}{K_0} = \frac{\rho_v}{\rho_0} (l + \beta t)^n e^{-at}$$

*At low temperatures negative temperature coefficients* have been found in very few instances. As was stated before, we have found *negative* temperature coefficients in the case of cobalt chloride in acetone; in a 75 per cent mixture of acetone with methyl alcohol; also in 50 and 75 per cent mixtures of acetone with ethyl alcohol. In the 75 per cent mixture of acetone with methyl alcohol, at the dilution  $v = 200$ , we have practically a *zero temperature coefficient of*

<sup>1</sup> Proc. Roy. Soc., **71**, 42 (1902).

<sup>2</sup> Beibl., **16**, 182 (1892).

*conductivity.* In all cases these negative coefficients were found while working at *ordinary temperatures.*

Acetone and the alcohols are considered to be highly associated compounds at ordinary temperatures. We have shown that the diminishing dissociating power of a solvent with rise in temperature, must overcome the increasing velocities of the ions in order to have a decrease in conductivity with rise in temperature. Acetone and the alcohols are more associated at  $0^{\circ}$  than at  $25^{\circ}$  and, consequently, their dissociating power is greater at the lower temperature. The ions, however, move faster at  $25^{\circ}$  than at  $0^{\circ}$ . Since we have found negative temperature coefficients, we believe that the effect due to diminishing dissociation more than overcomes the effect due to the increasing velocities of the ions.

We think, nevertheless, that there is another factor which comes into play. We are inclined to the view that the solvates which are formed in these cases may be more stable at the higher temperature and, therefore, we should expect the reaction which gave rise to them to be endothermic. At the dilution where the temperature coefficient of conductivity is practically zero, these *opposite influences which affect conductivity become equal.* The point where we have a temperature coefficient which is practically zero corresponds to the maximum in conductivity obtained by other workers at high temperatures.

#### SUMMARY.

(1) We have measured the fluidities of water, methyl alcohol, ethyl alcohol, acetone, and binary mixtures of these solvents; also the fluidities of solutions of lithium bromide in these mixtures.

(2) We have also measured the conductivity of various concentrations of lithium bromide and cobalt chloride, in the above-named solvents and mixtures of these with one another.

(3) The conductivities, in the case of mixtures of the alcohols with water, exhibit a minimum. The same fact was found to be true in the case of mixtures of acetone with water. This minimum in conductivity was found to be more pronounced at the lower temperature, and has been shown to be intimately connected with the minimum in fluidity observed in the above mixtures.

(4) The conductivities of lithium bromide, in mixtures of methyl and ethyl alcohols, are what we should expect from the law of averages. The conductivity curves are nearly straight lines. In the case of cobalt chloride, in these mixtures, there was a slight sagging of the curves.

(5) In the case of lithium bromide, in mixtures of acetone with the alcohols, the fluidities are what we should expect from the law of averages — the fluidity curves are straight lines. The same has been found to be true in the case of the pure solvents. This indicates that acetone and the alcohols do

not form more complex aggregations when mixed than when unmixed. Here, again, conductivity has been shown to be connected with fluidity.

(6) Lithium bromide, however, gives a pronounced maximum in conductivity, in mixtures of acetone with methyl or ethyl alcohol. The same phenomenon was observed in the case of cobalt chloride in mixtures of acetone with ethyl alcohol. We believe this maximum is due, primarily, to a diminution in the dimensions of the atmosphere about the ions.

(7) We think, also, that the changes in the size of the ionic spheres should be considered as a factor in causing the conductivity minimum as well as the maximum.

(8) We have determined the temperature coefficients of conductivity and fluidity, and found them to be of the same order of magnitude. Lithium bromide, in the mixtures studied, showed, with rise in temperature, a large increase in conductivity, due to increase in fluidity. The temperature coefficients of lithium bromide in the above mixtures are, therefore, all positive.

(9) Cobalt chloride, however, in some of the acetone mixtures, at *ordinary temperatures*, gave *negative temperature coefficients*. We think this is due not only to the effect of the diminishing dissociation more than overcoming the effect due to the increasing velocity of the ions, but also to the fact that the solvates formed in these cases may be more stable at the higher temperature. We should, therefore, expect the reaction which gave rise to the solvates to be endothermic.

(10) We have found for our substances, in a given mixture of solvents, a dilution where the temperature coefficient of conductivity is practically zero. This corresponds to the maximum in conductivity observed by other workers at elevated temperatures.

(11) We have shown that the temperature coefficients generally increase with the dilution, not only in aqueous solutions, but also in the non-aqueous solutions thus far studied.

## WORK OF VEAZEY.

### EXPERIMENTAL.

#### APPARATUS.

#### CONDUCTIVITY.

The conductivity measurements were made by the Kohlrausch method, using a Wheatstone bridge, induction coil, and telephone receiver.

The bridge-wire, which was of "magnanin," was carefully calibrated by the method of Strouhal and Barus,<sup>1</sup> and was found to have practically uniform resistance throughout its entire length.

All readings were taken within 100 mm. of either side of the center of the wire.

The resistance coils were made by Leeds & Co. and were accurate to within 0.04 per cent.

The conductivity cells were those used by Jones and Bingham<sup>2</sup> and by Jones and McMaster.<sup>3</sup> These cells were found to be very satisfactory. The cell constants in no case varied more than one unit in twelve months' continual use.

The zero-bath was prepared in the following manner: A porcelain enameled bucket, of about  $1\frac{1}{2}$  gallons capacity, was filled with finely crushed ice moistened with pure water. This vessel was placed in a fibroid bucket of 3 gallons capacity, the intervening space between the two being filled with ice and water as above described.

The bath thus prepared was found, when tested with a standard thermometer, to vary from the desired temperature not more than  $0.05^{\circ}$ , and to remain practically constant for at least 5 hours.

The  $25^{\circ}$  bath consisted of a round galvanized-iron vessel, of about 20 liters capacity, filled with water. The bath was stirred by means of a small propeller, driven by a Heinrich hot-air motor.

The thermometers used were graduated to  $0.2^{\circ}$ , and were carefully standardized by comparison with a thermometer which was tested at the "Reichsanstalt."

All burettes and flasks used in the preparation of solutions were carefully calibrated at  $20^{\circ}$ .

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<sup>1</sup> Wied. Ann., **10**, 326 (1880).

<sup>2</sup> Amer. Chem. Journ., **34**, 493 (1905).

<sup>3</sup> Ibid., **36**, 331 (1906).

VISCOSITY.

The viscometer used was a modified form of the one described by Ostwald and Luther.<sup>1</sup> The form described by them was found to be unsatisfactory for liquids having a much greater viscosity than water. The most serious objections are:

(1) The small capillary, above and below the bulb, renders it impossible to make an accurate observation of the meniscus of the descending column of liquid as it passes the mark.

(2) In case a liquid more viscous than water is used, the small capillary invariably fails to drain perfectly, and the liquid bridges over the capillary just above the bulb, thus forming a sort of valve which renders the results of the measurement entirely inaccurate.

To overcome these difficulties the following modified form was made: A large capillary was placed above and below the bulb, and the small capillary was joined to it as shown in fig. 78. The upper bulb of the viscometer had a capacity of about 3 c. c., and the lower bulb a capacity of about 5 c. c. The liquid was raised from the lower to the upper bulb by means of an aspirating bottle, the air being dried over soda-lime. The time of flow through the capillary tube was determined by means of a stop-watch reading to fifths of a second. The stop-watch used was found to be accurate to one-fifth of a second. This was established by a number of comparative tests with other standard watches.

The specific gravity of the solution is needed in the calculation of its viscosity. For specific-gravity measurements a slightly modified form of the pycnometer employed by Jones and Bingham<sup>1</sup> was used. This form of pycnometer is shown in fig. 79. The modification consists in the elongation of the large bulb, which brings a larger surface of the pycnometer, per unit volume, in contact with the bath. The small bulb was made oval in shape so as to secure a better draining of the bulb, and the whole instrument was of much lighter construction and of somewhat greater capacity than that employed by Jones and Bingham.

The zero-bath consisted of a large glass cylinder filled with crushed ice moistened with water. It was found necessary to have the viscometer

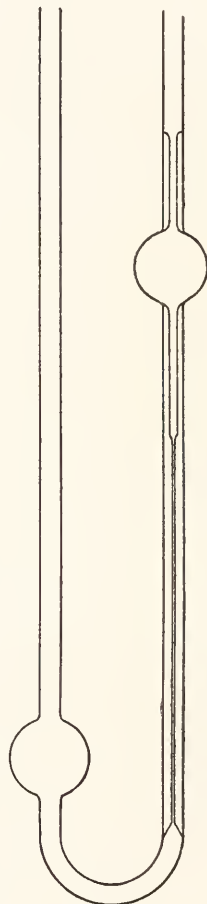


FIG. 78.

<sup>1</sup> Amer. Chem. Journ., 16, 479 (1894).

<sup>1</sup> Ibid., 34, 495 (1905).

placed at least 2 or 3 cm. from the walls of the bath, to insure uniform temperature; and to render the graduations on the viscometer more clearly visible

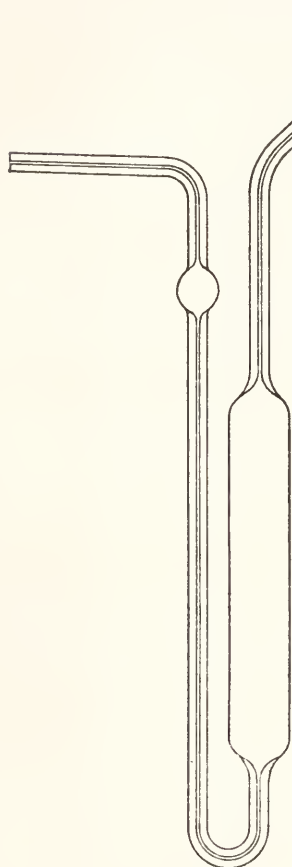


FIG. 79.

they were filled with India ink, which was then rendered insoluble by heating. The thermometer bulb was always placed *between the bulb of the viscometer and the wall of the bath*, in order to make certain that that portion of the bath was at the proper temperature. This precaution is necessary, since it was determined by a number of experiments that if any very large amount of water is allowed to collect next to the wall of the bath, its temperature may rise as much as one-half a degree above zero. With a little care, however, it was found possible to keep the portion of the bath immediately surrounding the viscometer constant to within less than one-tenth of one degree.

The 25° bath was similar to that described by Jones and McMaster.<sup>1</sup> It was found desirable to place a small quantity of potassium dichromate in this bath, since this not only prevented the accumulation of organic growth in the bath, but also the yellow color made the graduations on the instrument placed in the bath much more clearly visible. This bath was easily maintained constant to within one-tenth of a degree, by means of a small flame regulated by a Mohr pinchcock.

#### SOLVENTS.

##### WATER.

The water used was purified as follows: Ordinary distilled water was distilled from potassium dichromate and sulphuric acid. It was then distilled a second time from potassium dichromate and sulphuric acid, into barium hydroxide, from which it was finally distilled into a bottle which was protected from the carbon dioxide of the air and other impurities, by a tube filled

<sup>1</sup> Amer. Chem. Journ., 36, 333 (1906).

with soda lime. Water purified in this manner had a conductivity of from  $1 \times 10^{-6}$  to  $1.5 \times 10^{-6}$  at  $0^\circ$ , and from  $1.8 \times 10^{-6}$  to  $2.5 \times 10^{-6}$  at  $25^\circ$ .

#### METHYL ALCOHOL.

The methyl alcohol used was the best that could be obtained commercially. It was purified by boiling over calcium oxide for several days, and then distilled into a glass-stoppered bottle containing anhydrous copper sulphate, where it was allowed to stand for at least a month before using. To prepare the alcohol for final use, it was distilled from the copper sulphate into a bottle carefully protected from moisture, the first and last 150 c. c. of the distillate being discarded. The conductivity of the methyl alcohol thus prepared was practically the same as that of the water.

#### ETHYL ALCOHOL.

The ethyl alcohol was purified in the same manner as the methyl alcohol, and gave an average value for conductivity of from  $2 \times 10^{-7}$  to  $3 \times 10^{-7}$  at  $0^\circ$ , and from  $5 \times 10^{-7}$  to  $7 \times 10^{-7}$  at  $25^\circ$ .

#### ACETONE.

The acetone was dried over fused calcium chloride for about one month, and then distilled immediately before using, in the same manner as the alcohol. Its average conductivity was about  $3 \times 10^{-7}$  at  $0^\circ$ , and  $4 \times 10^{-7}$  at  $25^\circ$ .

#### SOLUTIONS.

In making up the mixed solvents and in diluting the solutions to any given volume, care was taken to bring all solvents and solutions to exactly  $20^\circ$  before making the measurements or dilutions. In all cases when one solvent was mixed with another, or a salt was dissolved in a solvent, the solution was brought to  $20^\circ$  before making up to the complete volume. The mixed solvents were made up as designated by Jones and Bingham,<sup>1</sup> *i. e.*, " $x$  c. c. of acetone diluted to 100 c. c. was designated as a mixture of  $x$  per cent acetone."

The mother-solutions were prepared by weighing the salt directly into the measuring flask and diluting with the solvent to a known volume. From this mother-solution the other solutions were prepared by dilution to the desired volume. Whenever this would require the use of less than 5 c. c. of the mother-solution, a more dilute mother-solution was prepared, and from this the successive dilutions were made.

#### CONDUCTIVITY MEASUREMENTS.

Four readings were taken with each solution, using a different resistance for each reading. The cell constants were determined in the usual way by

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<sup>1</sup> Amer. Chem. Journ., **34**, 494 (1905).

the use of N/50 and N/500 solutions of potassium chloride. The value used for N/50 potassium chloride at 25° was 129.7. The value for N/500 potassium chloride was determined every time a fresh solution of it was prepared, by first determining the cell constants of several cells with N/50 potassium chloride, and then using these cells to determine the value for N/500 potassium chloride. The cell constants were checked at frequent intervals. After use the cells were repeatedly rinsed with distilled water, and when not in use the cells were filled with distilled water. The cells before use were rinsed with water and then with absolute alcohol, and allowed to dry at ordinary temperatures.

The use of ether in drying the cells was avoided, since it is likely to contain small amounts of non-volatile substances.

In table 78  $v$  is the number of liters of solvent that contain 1 gram-molecular weight of the salt;  $\mu_v 0^\circ$  is the molecular conductivity at 0°, and  $\mu_v 25^\circ$  is the molecular conductivity at 25°.

The temperature coefficients were calculated according to the Kohlrausch formula, and, if multiplied by 100, would express the temperature coefficients in percentage of conductivity units. The Kohlrausch formula as it was applied is  $\frac{\mu_v 25^\circ - \mu_v 0^\circ}{25} \cdot \frac{1}{\mu_v 0^\circ}$ .

#### COBALT NITRATE.

A number of methods were used in an attempt to obtain perfectly anhydrous cobalt nitrate, but without success; and since it is absolutely necessary to have the salt completely anhydrous for this work, this salt had to be abandoned.

The most nearly successful attempt to dehydrate the salt was carried out as follows: The salt was heated several days to dryness on a water-bath, and was then recrystallized several times from strong nitric acid. The crystals were then washed with anhydrous ligroine to free them from the acid. They were then filtered and drained by the aid of a suction-pump, the funnel containing the crystals being carefully protected from the moisture of the air. The salt was then heated for a day or two in a current of dry air at a temperature of from 50° to 60°. An analysis of the sample thus obtained, for metallic cobalt by the electrolytic method, showed that the salt still contained a considerable amount of water.

#### COPPER CHLORIDE.

The copper chloride used in this work was prepared as follows: Kahlbaum's pure crystallized copper chloride was recrystallized from dilute hydrochloric acid to free it from small quantities of basic salt. These crystals were then



dehydrated by heating in a current of dry hydrochloric acid, at a temperature of from  $140^{\circ}$  to  $150^{\circ}$ , to constant weight. The salt was then placed in a vacuum desiccator over sulphuric acid and potassium hydroxide, to remove any traces of hydrochloric acid. The salt had a dark-brown color, and gave perfectly clear solutions when dissolved in the water or the alcohols. The salt was analyzed by the electrolytic method, using a rotating anode. The results of the analysis agreed with the calculated result for pure copper chloride to within 0.05 per cent. The salt was preserved in glass-stoppered bottles over phosphorus pentoxide.

The results obtained in the mixture of methyl alcohol and water were not entirely satisfactory, because of the formation in the 50 per cent, and more especially in the 75 per cent mixtures, of a cloudiness in the solutions within a few minutes after dissolving the salt. This was probably due to a partial reduction of the salt by the alcohol in the presence of water, since no such action could be observed in either the methyl alcohol or the aqueous solutions. The conductivity of the solutions in which the cloudiness appeared was determined without filtering the solution, and after 24 hours the conductivity of the solution was again determined. No appreciable change in the conductivity could be detected, showing that the change in the solution proceeded rapidly at first and soon reached the equilibrium point.

An attempt was made to determine the conductivity of copper chloride in acetone, and mixtures of acetone with other solvents, but there was a very appreciable action between the salt and the acetone, and, consequently, work in this field was given up. There was not only a very rapid change in the conductivity of the acetone solutions of copper chloride, so that it was impossible to duplicate results; but the molecular conductivity varied with the dilution in a peculiar manner — becoming greater with increase in dilution from  $N/100$  to  $N/200$ , and then decreasing from  $N/200$  to  $N/800$ , where the values reached a minimum, and then increasing again from  $N/800$  to  $N/1600$ .

The solutions changed color slowly on standing for some time, and when the solvent was distilled off on a water-bath apparently an organo-metallic compound remained in the flask, which had none of the properties of either cupric or cuprous chloride.

Table 78, for copper chloride, in mixtures of methyl alcohol and water, when plotted as curves (figs. 80 and 81), shows that there is a decided drop in the curves below the rule of averages, and that this drop in the curve is most pronounced in the 50 per cent mixtures. The values between 75 per cent and 100 per cent mixtures are practically in accord with the rule of averages, at  $25^{\circ}$ , and have a general tendency in the same direction at  $0^{\circ}$ .

It is also to be observed that the values for the conductivity in methyl alcohol are very much smaller than the corresponding values in water.

TABLE 78. — *Conductivity of copper chloride at 0° and 25°.*

$\nu$	In water.			In 25 p. ct. methyl alcohol and water.			In 50 p. ct. methyl alcohol and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
10	89.28	162.60	0.03285	48.12	98.73	0.0421	35.35	68.27	0.0372
50	103.94	193.87	.03461	56.57	119.03	.0442	43.92	88.14	.0403
100	106.14	204.86	.03720	59.96	128.00	.0454	46.99	95.63	.0414
200	115.03	214.87	.03471	52.14	133.80	.0461	50.14	102.24	.0416
400	117.47	220.34	.03503	65.36	141.60	.0467	53.22	110.48	.0430
800	123.73	231.03	.03469	67.45	146.90	.0471	54.91	114.56	.0435
1600	129.52	249.70	.03712	67.37	147.30	.0475	59.01	123.50	.0437

$\nu$	In 75 p. ct. methyl alcohol and water.			In methyl alcohol.			In 25 p. ct. ethyl alcohol and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
10	30.28	48.20	0.0237	15.04	17.98	0.00984	34.45	81.17	0.0543
50	42.17	69.75	.0262	27.28	32.98	.00936	40.50	99.17	.0578
100	47.95	80.59	.0272	33.58	42.37	.01047	43.27	107.01	.0589
200	52.48	89.97	.0286	40.46	50.06	.00949	45.12	112.44	.0597
400	57.06	99.83	.0300	46.36	57.78	.00985	46.31	116.73	.0608
800	59.87	106.13	.0309	53.51	65.78	.00917	47.45	119.85	.0610
1600	63.67	114.25	.0318	60.25	72.64	.00823	49.06	126.90	.0635

$\nu$	In 50 p. ct. ethyl alcohol and water.			In 75 p. ct. ethyl alcohol and water.			In ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
10	19.66	46.98	0.0556	13.24	25.17	0.0360	3.53	4.88	0.0153
50	24.41	61.24	.0604	18.64	36.83	.0390	6.42	8.30	.0117
100	26.60	67.56	.0616	21.20	42.46	.0401	8.48	12.07	.0169
200	28.28	73.05	.0633	24.17	48.81	.0408	10.20	13.59	.0133
400	29.79	77.84	.0645	26.33	53.92	.0419	12.01	17.18	.0172
800	30.87	81.43	.0655	28.25	59.05	.0436	13.95	19.92	.0171
1600	32.57	88.16	.0683	32.36	67.31	.0432	15.91	25.24	.0235

$\nu$	In 25 p. ct. methyl alcohol and ethyl alcohol.			In 50 p. ct. methyl alcohol and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	5.12	6.39	0.00992	7.81	0.57	0.00901
50	9.63	11.83	.00914	14.68	18.09	.00929
100	12.35	15.48	.01014	18.43	23.21	.01037
200	15.16	17.47	.00610	22.39	28.94	.01170
400	18.17	24.18	.01320	26.54	35.54	.01356
800	20.76	28.58	.01510	29.77	40.70	.01469
1600	23.97	34.90	.01830	34.83	48.90	.01616

$\nu$	In 75 p. ct. methyl alcohol and ethyl alcohol.			In ethyl alcohol and water.				
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	11.44	13.88	0.00853	0.0329	0.0543	0.0556	0.0360	0.0153
50	21.10	25.93	.00916	.0346	.0578	.0604	.0390	.0117
100	26.08	32.61	.01002	.0372	.0589	.0616	.0401	.0169
200	31.28	39.98	.01113	.0347	.0597	.0633	.0408	.0133
400	37.33	48.80	.01229	.0350	.0608	.0645	.0419	.0172
800	40.95	53.75	.01250	.0347	.0610	.0655	.0436	.0171
1600	48.76	64.12	.01260	.0371	.0635	.0683	.0432	.0235

In studying the temperature coefficients of conductivity, it is to be noted that in every case, with the exception of pure methyl alcohol, there is an increase in the temperature coefficient with increase in dilution. This increase, although not perfectly regular, is, however, decidedly marked when the difference in the value for the most concentrated and for the most dilute solution is considered. It is also to be observed that the temperature coefficients in the 25 per cent mixture are decidedly larger than the corresponding values in either of the other mixtures used.

TABLE 79. — Comparison of the conductivities of copper chloride.

<i>v</i>	In mixtures of methyl alcohol and water at 0°.					In mixtures of methyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	89.28	48.12	35.35	30.28	15.04	162.60	98.73	68.27	48.20	17.98
50	103.94	56.57	43.92	42.07	27.28	193.87	119.03	88.14	69.75	32.98
100	106.14	59.96	46.99	47.95	33.58	204.86	128.00	95.63	80.59	42.37
200	115.03	62.14	50.14	52.48	40.46	214.84	133.80	102.24	89.97	50.06
400	117.47	65.36	53.22	57.06	46.36	220.34	141.60	110.48	99.82	57.78
800	123.73	67.45	54.91	59.87	53.51	231.03	146.90	114.56	106.13	65.78
1600	129.52	67.37	59.01	63.61	60.25	249.70	147.30	123.50	114.25	72.64

<i>v</i>	In mixtures of ethyl alcohol and water at 0°.					In mixtures of ethyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	89.28	34.45	19.66	13.24	3.53	162.60	81.17	46.98	25.17	4.88
50	103.98	40.50	24.41	18.64	6.42	193.87	99.17	61.24	36.83	8.30
100	106.14	43.27	26.60	21.20	8.48	204.86	107.01	67.56	42.46	12.07
200	115.03	45.12	28.28	24.17	10.20	214.84	112.44	73.05	48.81	13.59
400	117.47	46.31	29.79	26.33	12.01	220.34	116.73	77.84	53.92	17.18
800	123.73	47.45	30.87	28.25	13.95	231.03	119.85	81.43	59.05	19.92
1600	129.52	49.06	32.57	32.36	15.91	249.70	126.90	88.16	67.31	25.24

<i>v</i>	In mixtures of methyl alcohol and ethyl alcohol at 0°.					In mixtures of methyl alcohol and ethyl alcohol at 25°.				
	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.
10	3.53	51.2	7.81	11.44	15.04	4.88	6.39	9.57	13.88	17.98
50	6.42	96.3	14.68	21.10	27.28	8.30	11.83	18.09	25.93	32.98
100	8.48	123.5	18.43	26.08	33.58	12.07	15.48	23.21	32.61	42.37
200	10.20	151.6	22.39	31.28	40.46	13.59	17.47	28.94	39.98	50.06
400	12.01	181.7	26.54	37.33	46.36	17.18	24.18	35.54	48.80	57.78
800	13.95	207.6	29.77	40.95	53.51	19.92	28.58	40.70	53.75	56.78
1600	15.91	239.7	34.83	48.76	60.25	25.24	34.94	48.90	64.12	72.64

Tables 78 and 79 (figs. 82 and 83) show that copper chloride, in mixtures of ethyl alcohol and water, also gives a dropping below the rule of averages for the curves in the 25 per cent and 50 per cent mixtures. Here also, the values between the 75 per cent and 100 per cent mixtures show a general tendency towards the rule of averages. It is to be noted also that there is a bunching of the curves in the 25 per cent and the 51 per cent mixtures, or,

in other words, that there is a comparatively small increase in conductivity with increase in dilution in these mixtures. It is further to be observed that the conductivity values in ethyl alcohol are very much smaller than those in water, although the general increase in conductivity with increase in dilution is about the same in both cases.

The temperature coefficients of conductivity in every case increase with

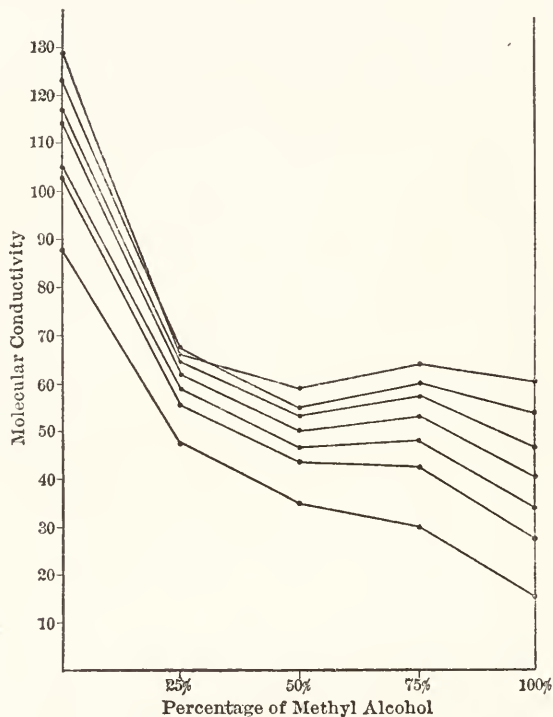


FIG. 80. — CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 0°.

TABLE 80. — Comparison of the temperature coefficients of conductivity of copper chloride.

$\nu$	In mixtures of methyl alcohol and water from 0° to 25°.					In mixtures of methyl alcohol and ethyl alcohol from 0° to 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.
10	0.0329	0.0421	0.0372	0.0237	0.00984	0.0153	0.00992	0.00901	0.00853	0.00984
50	.0346	.0442	.0403	.0262	.00836	.0117	.00914	.00929	.00916	.00836
100	.0372	.0454	.0414	.0272	.01047	.0169	.01014	.01037	.10002	.01047
200	.0347	.0461	.0416	.0286	.00949	.0133	.00610	.01170	.01113	.00949
400	.0350	.0467	.0431	.0300	.00985	.0172	.01320	.01356	.01229	.00985
800	.0347	.0471	.0435	.0309	.00917	.0171	.01510	.01469	.01250	.00917
1600	.0371	.0475	.0437	.0318	.00823	.0235	.01830	.01616	.01260	.00823

increase in dilution, not with any great regularity, but the values for the most dilute solutions are decidedly greater than those for the most concentrated. Here again, we note that temperature coefficients are larger in the mixtures than they are in either of the pure solvents, and that these values are on the whole largest in the 50 per cent mixture instead of in the 25 per cent, as was the case with methyl alcohol and water.

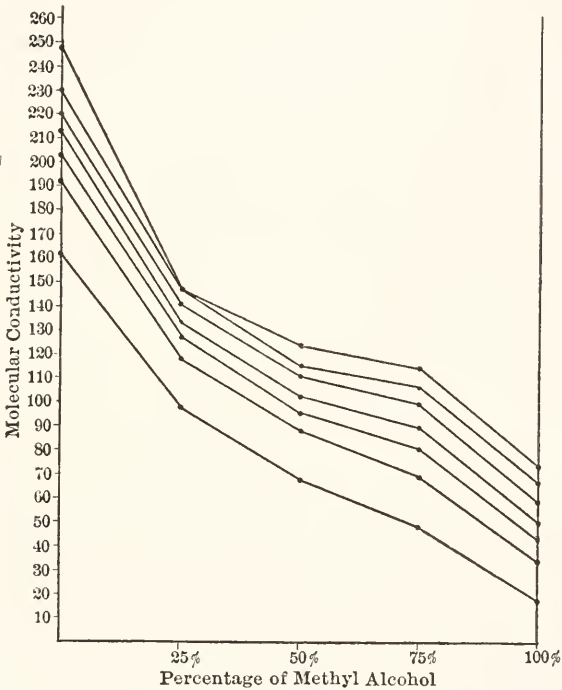


FIG. 81.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 25°.

Tables 78 and 79 (figs. 84 and 85) show that copper chloride, in mixtures of methyl alcohol and ethyl alcohol, gives no minimum in conductivity, but it is to be noted that there is a *decided dropping of the values in the 25 per cent and 50 per cent mixtures*, below the values calculated from the rule of averages, and that this is less pronounced in the more concentrated solutions than in the dilute. A slight exception is found in the case of the N/1600 solution at 25°, where a slight increase in the value above the average value is to be observed in the 75 per cent mixture. The remainder of the curve shows the same decrease in values as is shown by the other curves. Here again it is to be noted that the conductivity values in ethyl alcohol are much smaller than those in methyl alcohol, and increase much less rapidly with the dilution.

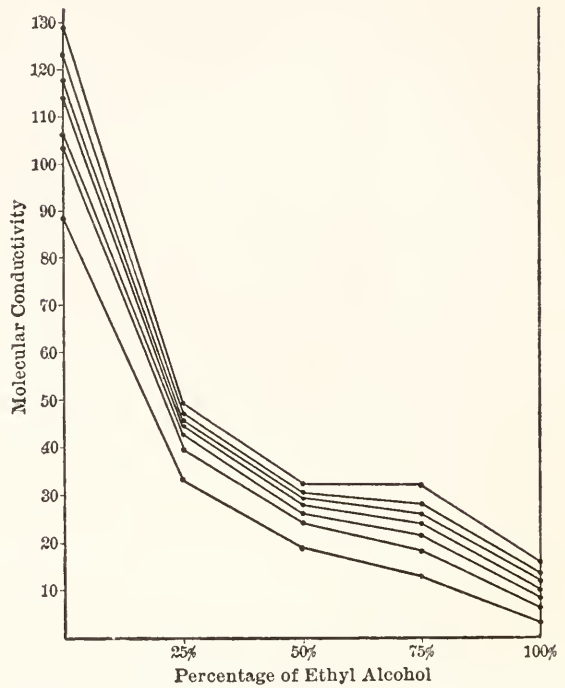


FIG. 82. — CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 0°.

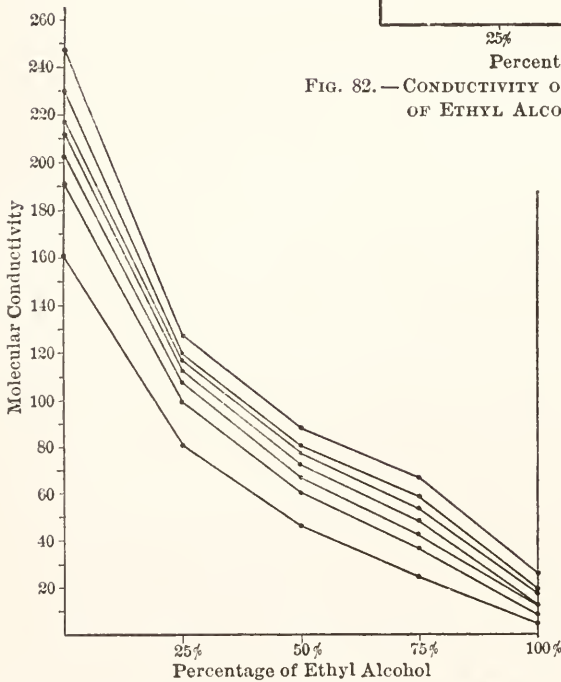


FIG. 83. — CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°.

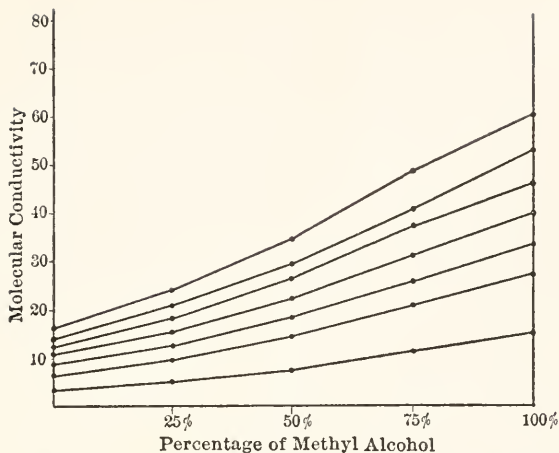


FIG. 84.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 0°.

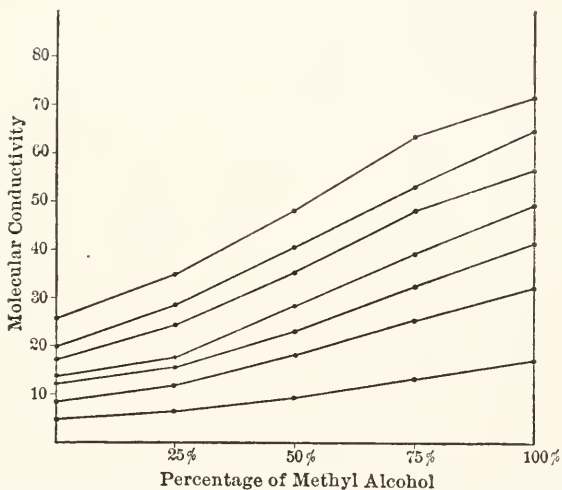


FIG. 85.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 25°.

POTASSIUM SULPHOCYANATE.

The potassium sulphocyanate used in this work was purified in the following manner: The purest salt obtainable was twice recrystallized from redistilled, 95 per cent ethyl alcohol, and then once recrystallized from absolute alcohol. The crystals were drained by suction, and dried at 100°. In every case the salt was crystallized in as finely divided condition as possible. The salt was preserved in glass-stoppered bottles, in a sulphuric acid desiccator.

TABLE 81. — *Conductivity of potassium sulphocyanate at 0° and 25°.*

$\nu$	In water.			In a mixture of 25 p. ct. methyl alcohol and water.			In a mixture of 50 p. ct. methyl alcohol and water.		
	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.	$\mu_{\nu}0^{\circ}$	$\mu_{\nu}25^{\circ}$	Temperature coefficient.
10	62.98	112.70	0.0316	37.04	75.00	0.0410	29.59	59.19	0.0400
50	67.42	121.44	.0321	39.09	80.35	.0422	31.35	63.59	.0411
100	68.78	125.06	.0327	39.45	81.14	.0423	31.78	64.62	.0413
200	69.73	126.47	.0326	40.31	82.86	.0422	32.53	66.47	.0417
400	71.62	129.99	.0326	41.19	84.94	.0425	32.63	66.93	.0421
800	71.42	128.96	.0322	41.97	85.29	.0413	32.85	68.17	.0430
1600	72.64	121.61	.0325	41.94	85.84	.0419	33.72	69.87	.0429
$\nu$	In a mixture of 75 p. ct. methyl alcohol and water.			In methyl alcohol.			In a mixture of 25 p. ct. ethyl alcohol and water.		
10	32.06	56.46	0.0304	46.83	64.81	0.0154	27.28	62.60	0.0518
50	35.21	62.77	.0313	56.94	79.40	.0158	28.14	65.90	.0537
100	36.22	64.86	.0316	60.63	84.97	.0161	28.73	67.88	.0545
200	27.34	67.37	.0322	63.78	89.91	.0164	29.51	69.71	.0545
400	37.96	68.75	.0324	66.01	92.91	.0163	29.57	70.73	.0557
800	37.74	70.10	.0343	68.80	97.19	.0165	29.49	71.70	.0573
1600	37.16	69.88	.0352	71.94	102.41	.0169	28.56	71.43	.0600
$\nu$	In a mixture of 50 p. ct. ethyl alcohol and water.			In a mixture of 75 p. ct. ethyl alcohol and water.			In ethyl alcohol.		
10	16.93	41.92	0.0590	15.43	32.73	0.0449	14.72	22.97	0.0224
50	17.39	44.37	.0621	16.66	36.31	.0472	18.97	30.13	.0235
100	17.84	45.79	.0627	17.32	37.89	.0475	20.74	33.15	.0239
200	18.02	46.36	.0629	17.76	39.06	.0480	22.45	36.20	.0245
400	18.23	46.94	.0630	17.95	39.70	.0485	23.66	38.82	.0256
800	18.39	47.13	.0625	18.21	40.34	.0486	24.88	41.02	.0260
1600	18.36	47.56	.0636	18.64	41.38	.0490	25.58	42.73	.0268
$\nu$	In a mixture of 25 p. ct. methyl alcohol and ethyl alcohol.			In a mixture of 50 p. ct. methyl alcohol and ethyl alcohol.			In a mixture of 75 p. ct. methyl alcohol and ethyl alcohol.		
10	21.09	31.85	0.0204	28.60	41.69	0.0183	37.06	52.40	0.0166
50	26.47	40.36	0.0210	35.56	52.08	.0186	45.39	64.85	.0172
100	28.89	44.27	0.0213	38.55	56.98	.0191	48.95	70.42	.0175
200	30.89	47.66	0.0217	40.77	60.30	.0192	51.29	74.17	.0178
400	32.32	50.39	0.0222	42.74	64.12	.0200	54.09	78.17	.0178
800	33.37	52.20	0.0226	43.94	66.10	.0202	54.95	79.75	.0181
1600	34.98	55.74	0.0237	45.40	69.09	.0209	57.55	83.61	.0181
$\nu$	In a mixture of 25 p. ct. acetone and water.			In a mixture of 50 p. ct. acetone and water.			In a mixture of 75 p. ct. acetone and water.		
10	39.47	78.74	0.0398	31.81	63.74	0.0402	34.59	59.07	0.0283
50	40.45	82.36	.0414	33.41	67.59	.0409	38.98	68.02	.0298
100	41.56	84.00	.0409	33.69	68.62	.0415	40.21	70.21	.0298
200	42.82	87.12	.0414	34.70	70.56	.0413	41.93	74.01	.0307
400	43.95	89.18	.0412	35.25	71.68	.0413	43.05	76.00	.0306
800	43.46	87.58	.0406	35.55	72.81	.0419	43.76	77.40	.0308
1600	43.59	87.56	.0404	36.86	76.62	.0432	44.00	78.48	.0312



TABLE 81.—*Conductivity of potassium sulphocyanate at 0° and 25°.*—Continued.

<i>v</i>	In acetone.			In a mixture of 25 p. ct. acetone and methyl alcohol.			In a mixture of 50 p. ct. acetone and methyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	43.44	48.66	0.00481	52.06	69.97	0.0138	53.92	70.51	0.0123
50	69.63	78.84	.00529	63.84	86.48	.0142	67.56	88.93	.0127
100	73.83	87.65	.00749	68.44	93.20	.0145	73.33	97.31	.0131
200	94.45	109.00	.00616	71.95	97.90	.0144	77.99	103.77	.0132
400	105.95	126.81	.00788	75.85	103.58	.0146	82.09	109.93	.0136
800	118.80	141.81	.00775	77.29	106.35	.0150	85.42	114.54	.0136
1600	126.20	151.92	.00815	79.75	101.11	.0157	88.41	119.41	.0140

<i>v</i>	In a mixture of 75 p. ct. acetone and methyl alcohol.			In a mixture of 25 p. ct. acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	57.40	71.33	0.00971	23.97	34.28	0.0172
50	74.50	93.21	.01005	30.86	44.55	.0177
100	81.96	104.08	.01080	34.13	49.59	.0181
200	86.53	111.05	.01133	36.43	53.55	.0188
400	94.19	120.98	.01138	38.74	57.54	.0194
800	98.00	126.14	.01148	40.55	60.58	.0198
1600	102.90	133.16	.01176	42.14	63.26	.0201

<i>v</i>	In a mixture of 50 p. ct. acetone and ethyl alcohol.			In a mixture of 75 p. ct. acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	34.62	45.51	0.0126	44.87	546.1	0.00868
50	45.06	60.17	.0134	59.92	744.1	.00967
100	49.92	67.40	.0140	67.52	850.6	.01039
200	53.52	73.13	.0147	72.90	925.1	.01076
400	57.35	79.11	.0152	78.97	1015.6	.01144
800	59.06	82.98	.0162	83.23	1078.6	.01184
1600	60.19	86.54	.0175	87.62	1147.3	.01237

TABLE 82.—*Comparison of the conductivities of potassium sulphocyanate.*

<i>v</i>	In mixtures of methyl alcohol and water at 0°.					In mixtures of methyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	62.98	37.04	29.59	32.06	46.83	112.70	75.00	59.19	56.46	64.81
50	67.42	39.09	31.35	35.21	56.94	121.44	80.35	63.59	62.77	79.40
100	68.78	39.45	31.78	36.22	60.63	125.06	81.14	64.62	64.86	84.97
200	69.73	40.31	32.53	37.34	63.78	126.47	82.86	66.47	67.37	89.91
400	71.62	41.19	32.63	37.96	66.01	129.99	84.94	66.93	68.75	92.91
800	71.42	41.97	32.85	37.74	68.80	128.96	85.29	68.17	70.10	97.19
1600	72.64	41.94	33.72	37.16	71.94	131.61	85.84	69.87	69.88	102.41

<i>v</i>	In mixtures of ethyl alcohol and water at 0°.					In mixtures of ethyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	62.98	27.28	16.93	15.43	14.72	112.70	62.60	41.92	32.73	22.97
50	67.42	28.14	17.39	16.66	18.97	121.44	65.90	44.37	36.31	30.13
100	68.78	28.73	17.84	17.32	20.74	125.06	67.88	45.79	37.89	33.15
200	69.73	29.51	18.02	17.76	22.45	126.47	69.71	46.36	39.06	36.20
400	71.62	29.57	18.23	17.95	23.66	129.99	70.73	46.94	39.70	38.82
800	71.42	29.49	18.39	18.21	24.88	128.96	71.70	47.13	40.34	41.02
1600	72.64	28.56	18.36	18.64	25.58	131.61	71.43	47.56	41.48	42.73

TABLE 82.—*Comparison of the conductivities of potassium sulphocyanate.*—Continued.

$\nu$	In mixtures of methyl alcohol and ethyl alcohol at 0°.					In mixtures of methyl alcohol and ethyl alcohol at 25°.				
	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.
10	14.72	21.09	28.60	37.06	46.83	22.97	31.85	41.69	52.40	64.81
50	18.97	26.47	35.56	45.39	56.94	30.13	40.36	52.08	64.85	79.40
100	20.74	28.89	38.55	48.95	60.63	33.15	44.27	56.98	70.42	84.97
200	22.45	30.89	40.77	51.29	63.78	36.20	47.66	60.30	74.17	80.91
400	23.66	32.31	42.74	54.09	66.01	38.82	50.39	64.12	78.17	92.91
800	24.88	33.37	43.94	54.95	68.80	41.02	52.20	66.10	79.75	97.19
1600	25.58	34.98	45.40	57.55	71.94	42.73	55.74	69.09	83.61	102.41

$\nu$	In mixtures of acetone and water at 0°.					In mixtures of acetone and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	62.98	39.47	31.81	34.59	43.44	112.70	78.74	63.74	59.07	48.66
50	67.42	40.45	33.41	38.98	69.63	121.44	82.36	67.59	68.02	78.84
100	68.78	41.56	33.69	40.21	73.83	125.06	84.00	68.62	70.21	87.65
200	69.73	42.82	34.70	41.93	94.45	126.47	87.12	70.56	74.10	109.00
400	71.62	43.95	35.25	43.05	105.95	129.99	89.18	71.68	76.00	126.81
800	71.42	43.46	35.55	43.76	118.80	128.96	87.58	72.81	77.40	141.81
1600	72.64	43.59	36.86	44.10	126.20	131.61	87.56	76.62	78.48	151.92

$\nu$	In mixtures of acetone and methyl alcohol at 0°.					In mixtures of acetone and methyl alcohol at 25°.				
	10	46.83	52.06	53.92	57.40	43.44	64.81	69.97	70.51	71.33
50	56.94	63.84	67.56	74.50	69.63	79.40	86.48	88.93	93.21	78.84
100	60.63	68.44	73.33	81.96	73.83	84.97	93.20	97.31	104.08	87.65
200	63.78	71.95	77.99	86.53	94.45	89.91	97.90	103.77	111.05	109.00
400	66.01	75.85	82.09	94.19	105.95	92.99	103.58	109.93	120.98	126.81
800	68.80	77.29	85.42	98.00	118.80	97.19	106.35	114.54	126.14	141.81
1600	71.94	79.75	88.41	102.90	126.20	102.41	111.11	119.41	133.16	151.92

$\nu$	In mixtures of acetone and ethyl alcohol at 0°.					In mixtures of acetone and ethyl alcohol at 25°.				
	10	14.72	23.97	34.62	44.87	43.44	22.97	34.28	45.51	54.61
50	18.97	30.86	45.06	59.92	69.63	30.13	44.55	60.17	74.41	78.84
100	20.74	34.13	49.92	67.52	73.83	33.15	49.59	67.40	85.06	87.65
200	22.45	36.43	53.52	72.90	94.45	36.20	53.55	73.13	92.51	109.00
400	23.66	38.74	57.35	78.97	105.95	38.82	57.54	79.11	101.56	126.81
800	24.88	40.55	59.06	83.23	118.80	41.02	60.58	82.98	107.86	141.81
1600	25.58	42.14	60.19	87.62	126.20	42.73	63.26	86.54	114.73	151.92

TABLE 83.—*Comparison of the temperature coefficients of conductivity of potassium sulphocyanate from 0° to 25°.*

$\nu$	In mixtures of methyl alcohol and water.					In mixtures of ethyl alcohol and water.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0316	0.0410	0.0400	0.0304	0.0154	0.0316	0.0518	0.0590	0.0449	0.0224
50	.0321	.0422	.0411	.0313	.0158	.0321	.0537	.0621	.0472	.0235
100	.0327	.0423	.0413	.0316	.0161	.0327	.0545	.0627	.0475	.0239
200	.0326	.0422	.0417	.0322	.0164	.0326	.0545	.0629	.0480	.0245
400	.0326	.0425	.0421	.0324	.0163	.0326	.0557	.0630	.0485	.0256
800	.0322	.0413	.0430	.0343	.0165	.0322	.0573	.0625	.0486	.0260
1600	.0325	.0419	.0429	.0352	.0169	.0325	.0600	.0636	.0490	.0268

TABLE 83.—*Comparison of the temperature coefficients of conductivity of potassium sulphocyanate from 0° to 25°.—Continued.*

<i>v</i>	In mixtures of methyl alcohol and ethyl alcohol.					In mixtures of acetone and water.				
	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0224	0.0204	0.0183	0.0166	0.0145	0.0316	0.0398	0.0402	0.0283	0.00481
50	.0235	.0210	.0186	.0172	.0158	.0321	.0414	.0409	.0298	.00529
100	.0239	.0213	.0191	.0175	.0161	.0327	.0409	.0415	.0298	.00749
200	.0245	.0217	.0192	.0178	.0164	.0326	.0414	.0413	.0307	.00616
400	.0256	.0222	.0200	.0178	.0163	.0326	.0412	.0413	.0306	.00788
800	.0260	.0226	.0202	.0181	.0165	.0322	.0606	.0419	.0308	.00775
1600	.0268	.0237	.0209	.0181	.0169	.0325	.0404	.0432	.0312	.00815

<i>v</i>	In mixtures of acetone and methyl alcohol.					In mixtures of acetone and ethyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0154	0.0138	0.0123	0.00971	0.00481	0.0224	0.0172	0.0126	0.00868	0.00481
50	.0158	.0142	.0127	.01005	.00529	.0235	.0177	.0134	.00967	.00529
100	.0161	.0145	.0131	.01080	.00749	.0239	.0181	.0140	.01039	.00749
200	.0164	.0144	.0132	.01133	.00616	.0245	.0188	.0146	.01076	.00616
400	.0163	.0146	.0136	.01138	.00788	.0256	.0194	.0152	.01144	.00788
800	.0165	.0150	.0136	.01148	.00775	.0260	.0198	.0162	.01184	.00775
1600	.0169	.0157	.0140	.01176	.00815	.0268	.0201	.0175	.01237	.00815

Tables 81 and 82 (figs. 86 and 87) show that potassium sulphocyanate gives a decided minimum in conductivity, for all the dilutions studied at 0°, in the 50 per cent mixtures of methyl alcohol and water; and that at 25° the

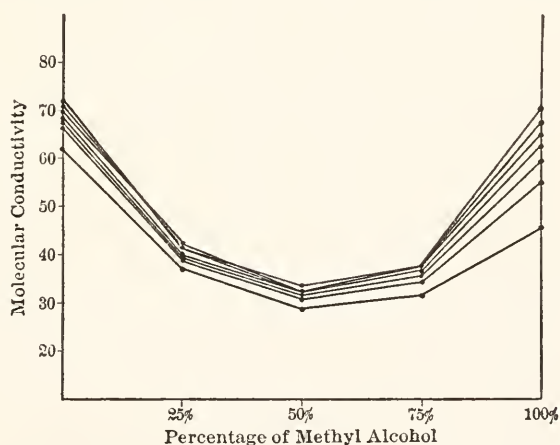


FIG. 86.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 0°.

minimum shifts its position in the first two dilutions to the 75 per cent mixture. It is also to be observed that in the mixtures there is but a very slight increase in molecular conductivity in the more dilute solutions, with increase in dilu-

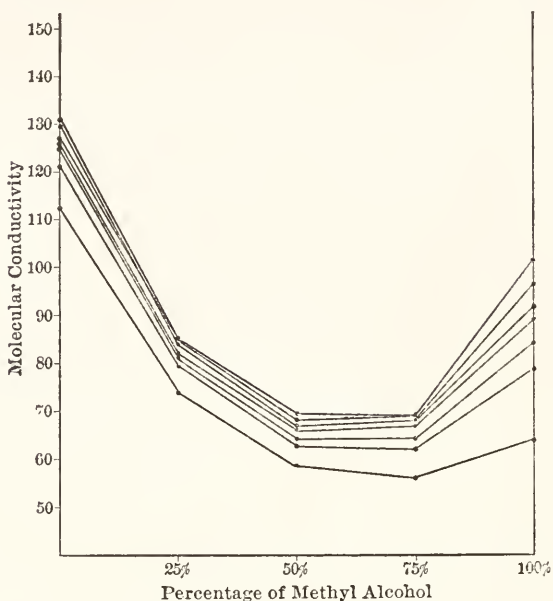


FIG. 87.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 25°.

tion. It is to be noted also that the increase in the conductivity with increase in dilution is greater in methyl alcohol than it is in water, although the values are considerably smaller.

The temperature coefficients of conductivity show in all cases a general increase with increase in dilution, and they are also larger in the 25 per cent and 50 per cent mixtures than in any of the other mixtures of the solvents.

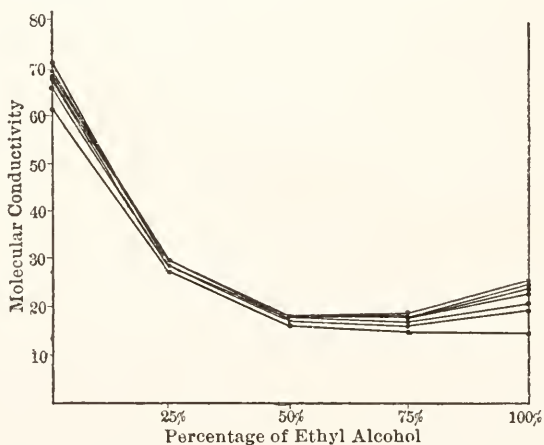


FIG. 88.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 0°.

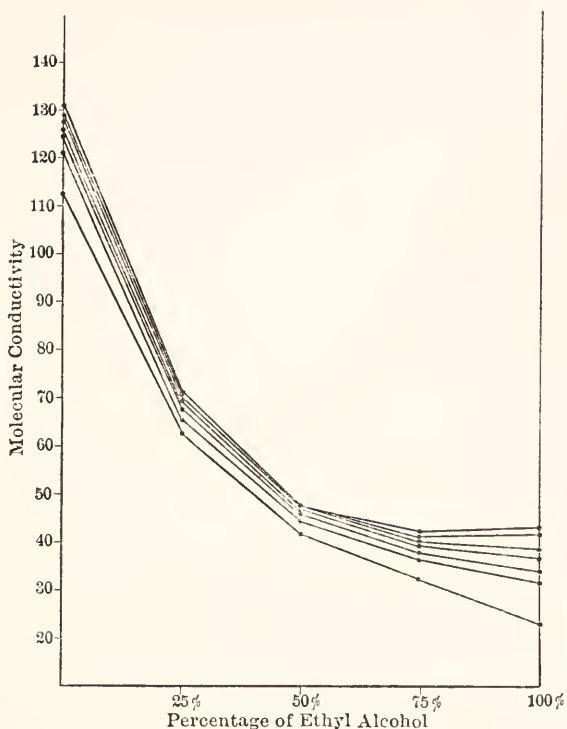


FIG. 89.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°.

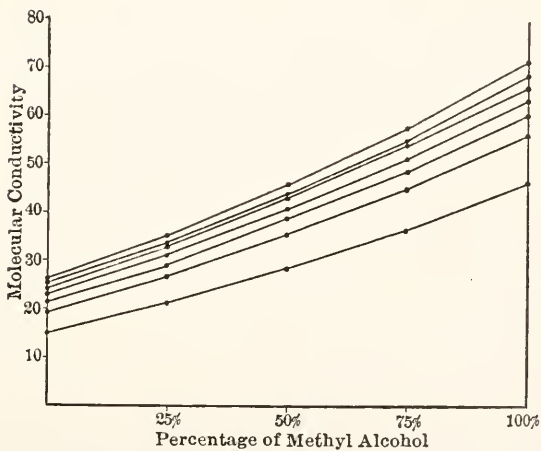


FIG. 90.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 0°.

Tables 81 and 82 (figs. 88 and 89) show that potassium sulphocyanate, in mixtures of ethyl alcohol and water, exhibits a minimum in conductivity at  $0^\circ$ , in the 50 and 75 per cent mixtures, in all cases except the N/10 solution, and at  $25^\circ$  the minimum is shown only in the N/800 and N/1600 solutions, in the 75 per cent mixture. The curves which do not show actual minima, exhibit a decided drop below the average values for the two solvents. They also show that there is only a very slight increase in conductivity with increase in dilution in the mixed solvents, and particularly in the 25 per cent and 50 per cent mixtures. It is to be noted, however, that the increase in conductivity with increase in dilution is greater in ethyl alcohol

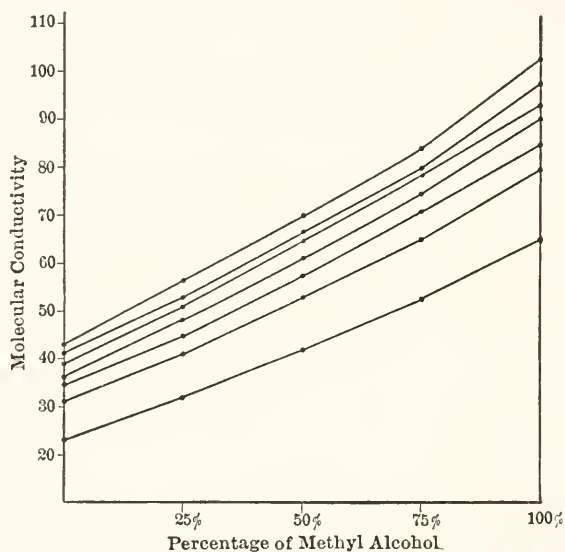
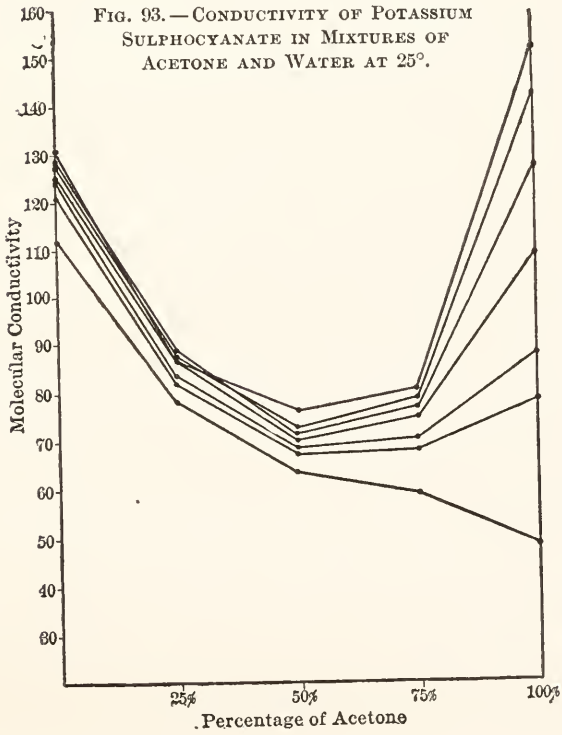
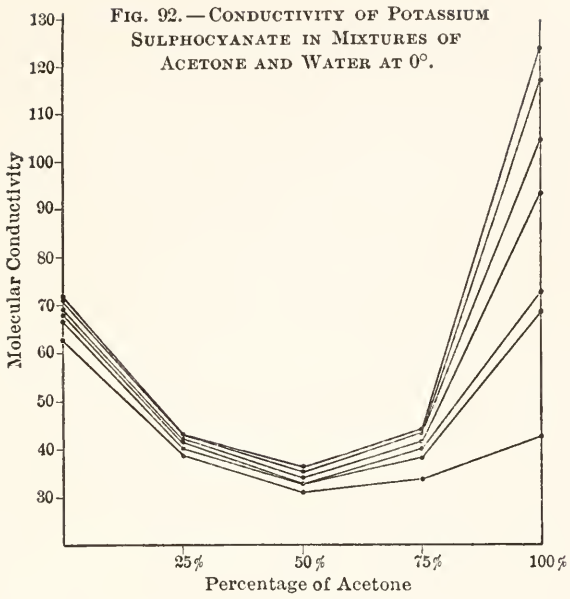


FIG. 91.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT  $25^\circ$ .

than it is in water for this particular salt. It is also to be noted that the actual value for conductivity in water is much greater than it is in ethyl alcohol. The temperature coefficients of conductivity show an increase with increase in the dilution of the solution, in every case, and these values are greatest in the 50 per cent mixture.

Tables 81 and 82 (figs. 90 and 91) show that potassium sulphocyanate, in mixtures of methyl alcohol and ethyl alcohol, does not exhibit a minimum in conductivity, but nevertheless there is an appreciable dropping of the curves, plotted from these values, below the average value. It is to be noted also that the increase in conductivity with increase in dilution is practically the average increase as calculated from the increase in the pure solvents. It is



also worthy of note that the conductivity values are greater in methyl alcohol than they are in ethyl alcohol. Here, again, there is a general increase in the value of the temperature coefficients with increase in the dilution of the solution, but in this case the temperature coefficients are greatest in ethyl alcohol and not in the mixtures.

Tables 81 and 82 (figs. 92 and 93) show that potassium sulphocyanate, in mixtures of acetone and water at  $0^{\circ}$ , exhibits, in all the dilutions studied, a decided minimum in conductivity. It is to be noted, however, that the minimum is somewhat less decided in the most concentrated solution (N/10).

At  $25^{\circ}$  the minimum occurs in all dilutions except N/10, where it entirely disappears. Here also in the more dilute solutions there is only a slight increase in conductivity, in the mixed solvents, with increase in dilution. It is also seen that even in the case where the minimum in conductivity has disappeared, there is a decided dropping of the curve below the average values. Also the increase in the conductivity in acetone, with increase in dilution, is very much greater than the corresponding increase in water. So great is this difference that although the values are less in acetone for the more concentrated solutions than the corresponding values in water, yet they become much greater in acetone than they do in water for the more dilute solutions.

The temperature coefficients show a general increase with increase in the dilution of the solutions, and the values of the temperature coefficients themselves are greatest in the 50 per cent mixture.

Tables 81 and 82 (figs. 94 and 95) show that potassium sulphocyanate, in mixtures of acetone and methyl alcohol, exhibits a maximum in conductivity in the 75 per cent mixture, for the first three dilutions (N/10, N/50, N/100) at  $0^{\circ}$ , and for the first four dilutions (N/10, N/50, N/100, N/200) at  $25^{\circ}$ . Also, that for the more dilute solutions the curves show a decided drop below the average values in the mixtures. It is also to be noted that the increase in conductivity with increase in dilution is very much greater in acetone than it is in methyl alcohol, and, further, that in all the mixtures the increase in conductivity with increase in dilution is practically what would be calculated from the law of averages. Here, again, we note a general increase in the temperature coefficients with increase in dilution, but in this case as in that of potassium sulphocyanate in methyl alcohol and ethyl alcohol, the greatest values do not occur in any of the mixtures, but in one of the pure solvents. In the case of acetone and methyl alcohol the greatest values are in pure methyl alcohol.

Tables 81 and 82 (figs. 96 and 97) show that potassium sulphocyanate, in mixtures of acetone and ethyl alcohol, exhibits a maximum in conductivity in the N/10 solution, in the 75 per cent mixture. However, there is a marked tendency towards a maximum and a very marked increase above the average values in N/50, N/100, and N/200 solutions. The remaining dilutions, while



they do not exhibit a true minimum, do, however, show a dropping below the average values in the mixtures. It is to be observed that the values for conductivity in acetone are much larger than the corresponding values for ethyl alcohol, and also, that the increase in conductivity with increase in dilution is very much larger in acetone than it is in ethyl alcohol. The increase in conductivity with dilution, in the mixtures, is, however, practically what would be calculated from the values in the pure solvents.

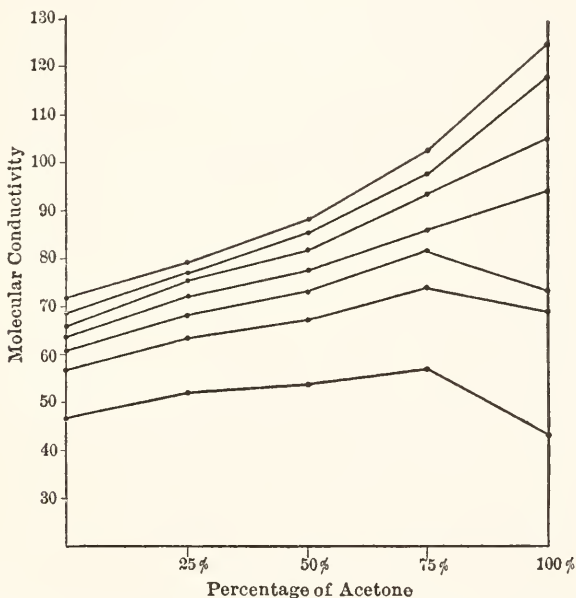
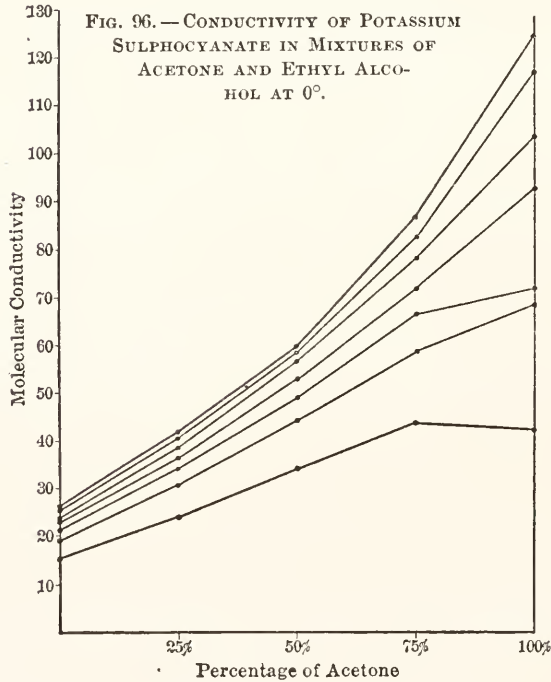
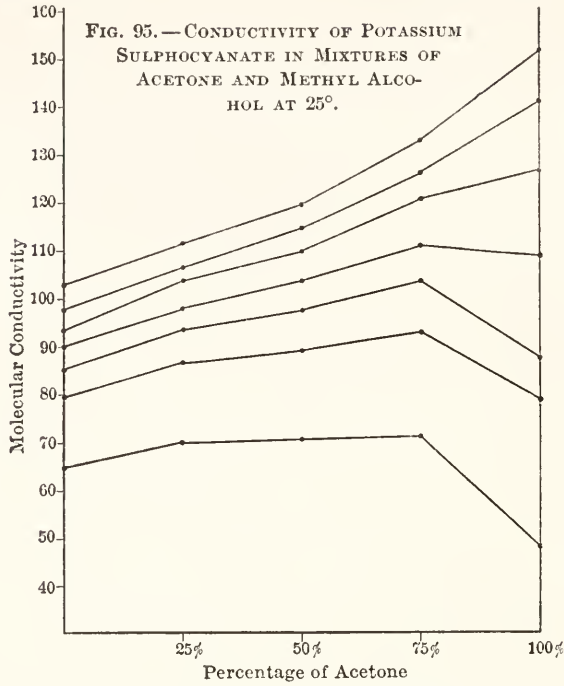


FIG. 94.— CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 0°.

Here, again, as in all the preceding cases, with a very few exceptions, we find a general increase in the temperature coefficients with increase in dilution. In this particular case the coefficients are largest in the pure solvent, ethyl alcohol, and not in the mixtures. A general examination of the temperature coefficients and conductivity in all of the pure solvents and mixtures thus far studied shows that although the increase in conductivity in acetone is relatively very large as compared with the increase in the other solvents, and that the temperature coefficients are relatively very small, yet the percentage increase in the temperature coefficients with increase in dilution is relatively large.



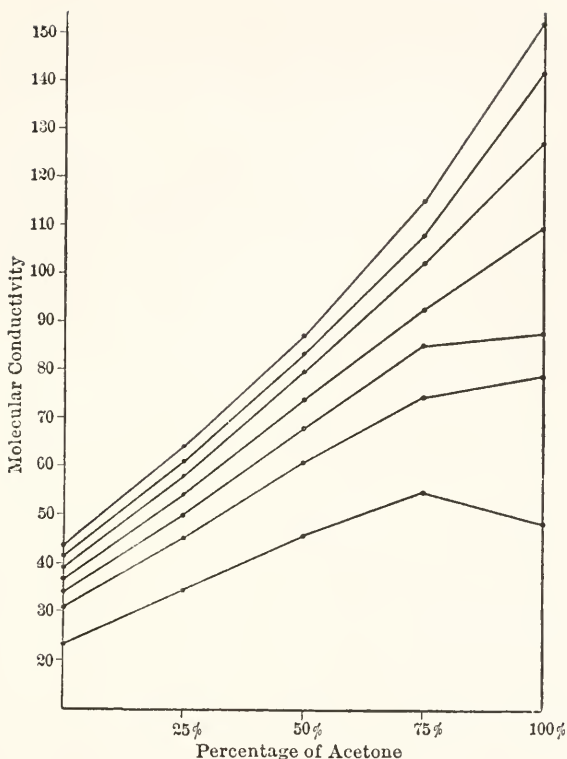


FIG. 97.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 25°.

VISCOSITY MEASUREMENTS.

The method used for measuring the viscosity of solutions throughout this work is that employed by Ostwald.<sup>1</sup> The viscosities have been calculated from the following formula :

$$n = n_0 \frac{St}{S_0 t_0}$$

in which  $n_0$  is the coefficient of viscosity for water,  $S_0$  is the specific gravity of water, and  $t_0$  the time of flow of water through any given capillary at a given temperature;  $n$  is the viscosity coefficient of the solution investigated,  $S$  is its specific gravity as compared with water as unity at any given temperature, and  $t$  is the time of flow of the given solution at that temperature. In the following tables the values for pure water at 0° and 25° were taken from the

<sup>1</sup> Ostwald-Luther: Physiko-chemische Messungen, Aufl. 2, p. 259.

work of Thorpe and Rodger,<sup>1</sup> and these values were used as the basis for the calculation of all the values given in tables 84 to 86.

The fluidity values were calculated from the following formula:

$$\phi = \frac{1}{n}$$

in which  $\phi$  is the fluidity, and  $n$  is the corresponding viscosity value. In other words, the fluidity values are simply the reciprocals of the viscosities. All the values given in tables 84 to 86 have been obtained both for pure solvents and solutions, using the modified form of viscometer which has been already described. Many of the values given have been carefully checked by using entirely different solutions in the several determinations.

TABLE 84. — *Fluidity of potassium sulphocyanate at 0° and 25°.*

Mixture.	$v$	$n_0^\circ$	$\phi_0^\circ$	$n_{25^\circ}$	$\phi_{25^\circ}$	Temperature coefficient.
In water . . . . .	10	0.01737	57.58	0.008823	113.34	0.0387
	1600	.....	.....	.008836	113.17	.....
	Solvent	.01778	56.24	.008910	112.23	.0398
25 p. ct. methyl alcohol and water . . . . .	10	.03203	31.22	.01297	77.08	.0588
	1600	.....	.....	.01310	76.34	.....
	Solvent	.03304	30.27	.01312	76.18	.0607
50 p. ct. methyl alcohol and water . . . . .	10	.03526	28.36	.01462	68.40	.0565
	1600	.....	.....	.01474	67.82	.....
	Solvent	.03586	27.89	.01477	67.72	.0571
75 p. ct. methyl alcohol and water . . . . .	10	.02479	40.35	.01201	83.24	.0425
	1600	.....	.....	.01197	83.56	.....
	Solvent	.02451	40.81	.01196	83.60	.0419
In methyl alcohol . . .	10	.009599	104.18	.006355	157.37	.0204
	1600	.....	.....	.006085	154.34	.....
	Solvent	.009032	110.72	.006084	165.36	.0194
25 p. ct. ethyl alcohol and water . . . . .	10	.04904	20.39	.01630	61.35	.0804
	1600	.....	.....	.01653	60.50	.....
	Solvent	.05135	19.47	.01661	60.19	.0837
50 p. ct. ethyl alcohol and water . . . . .	10	.06742	14.83	.02148	46.55	.0856
	1600	.....	.....	.02168	46.13	.....
	Solvent	.07005	14.27	.02170	46.08	.0892
75 p. ct. ethyl alcohol and water . . . . .	10	.04960	20.16	.01968	50.81	.0608
	1600	.....	.....	.01939	51.57	.....
	Solvent	.04996	20.01	.01935	51.68	.0633
In ethyl alcohol . . . .	10	.02237	44.71	.01261	79.28	.0309
	1600	.....	.....	.01197	83.54	.....
	Solvent	.02108	47.44	.01145	87.36	.0337

<sup>1</sup> Phil. Trans., 185A, 307 (1894).

TABLE 84.—*Fluidity of potassium sulphocyanate at 0° and 25°.*—Continued.

Mixture.	$v$	$n_0^\circ$	$\phi_0^\circ$	$n_{25^\circ}$	$\phi_{25^\circ}$	Temperature coefficient.
25 p. ct. acetone and water . . . . .	10	0.02849	35.10	0.01202	83.20	0.0548
	1600	.....	.....	.01206	82.92	.....
	Solvent	.02868	34.87	.01205	83.00	.0552
50 p. ct. acetone and water . . . . .	10	.03006	33.27	.01268	78.88	.0548
	1600	.....	.....	.01260	79.40	.....
	Solvent	.02992	33.42	.01258	79.52	.0552
75 p. ct. acetone and water . . . . .	10	.01737	57.58	.009000	111.11	.0372
	1600	.....	.....	.008763	114.12	.....
	Solvent	.01695	59.00	.008727	114.58	.0377
In acetone . . . . .	10	.005294	188.91	.004126	242.38	.01132
	1600	.....	.....	.004010	249.36	.....
	Solvent	.005045	198.24	.003977	251.46	.01074
25 p. ct. acetone and methyl alcohol . . . . .	10	.007429	134.61	.005380	185.86	.01522
	1600	.....	.....	.005115	195.49	.....
	Solvent	.006497	153.92	.005087	196.56	.0111
50 p. ct. acetone and methyl alcohol . . . . .	10	.005632	177.56	.004932	202.74	.00567
	1600	.....	.....	.004675	213.92	.....
	Solvent	.005177	193.16	.004498	222.33	.00604
75 p. ct. acetone and methyl alcohol . . . . .	10	.004726	211.62	.004567	218.99	.00139
	1600	.....	.....	.004253	235.12	.....
	Solvent	.004338	230.54	.004155	240.60	.00175
25 p. ct. methyl alcohol and ethyl alcohol . . . . .	10	.01707	58.58	.009892	101.10	.0290
	1600	.....	.....	.009500	105.27	.....
	Solvent	.01617	61.84	.009481	105.48	.0282
50 p. ct. methyl alcohol and ethyl alcohol . . . . .	10	.01341	74.56	.008270	120.91	.0249
	1600	.....	.....	.007905	126.51	.....
	Solvent	.01259	79.45	.008009	124.86	.0229
75 p. ct. methyl alcohol and ethyl alcohol . . . . .	10	.01059	94.46	.007115	140.56	.0195
	1600	.....	.....	.006791	147.24	.....
	Solvent	.01003	99.68	.006790	147.29	.0191
25 p. ct. acetone and ethyl alcohol . . . . .	10	.01302	76.80	.007808	128.07	.0267
	1600	.....	.....	.007617	131.29	.....
	Solvent	.01156	86.53	.007332	136.39	.0231
50 p. ct. acetone and ethyl alcohol . . . . .	10	.007934	126.04	.006027	165.92	.0127
	1600	.....	.....	.005377	185.98	.....
	Solvent	.007080	141.24	.005333	187.51	.0131
75 p. ct. acetone and ethyl alcohol . . . . .	10	.005353	186.81	.004663	214.45	.00592
	1600	.....	.....	.004453	224.57	.....
	Solvent	.004900	204.07	.004393	227.62	.00462

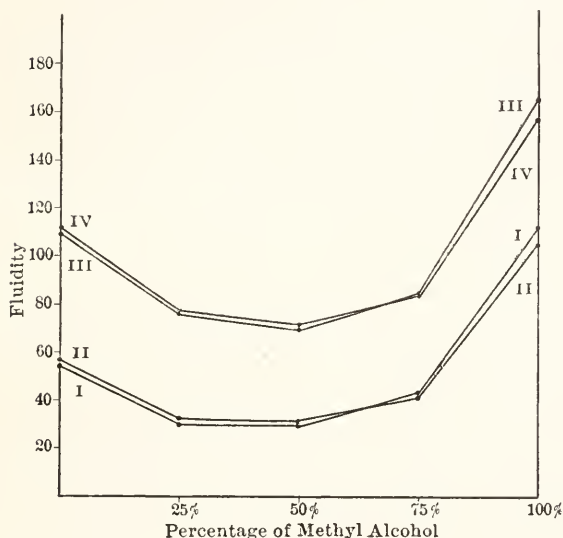
TABLE 85. — Comparison of fluidities of potassium sulphocyanate.

Mixture.	At —	$v$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	
Methyl alcohol and water . . . . .	0°	10	57.58	31.22	28.36	40.35	104.18	
		Solvent	56.24	30.27	27.89	40.81	110.72	
	25°	10	113.34	77.08	68.40	83.24	157.37	
		Solvent	113.17	76.34	67.82	83.56	164.34	
	Ethyl alcohol and water	0°	10	57.58	20.39	14.83	20.16	44.71
			Solvent	56.24	19.47	14.27	20.01	47.44
25°		10	113.04	61.35	46.55	50.81	79.28	
		Solvent	113.17	60.50	46.13	51.57	83.54	
Acetone and water . . . . .		0°	10	57.58	35.10	33.27	57.58	188.91
			Solvent	56.24	34.87	33.42	59.00	198.24
	25°	10	113.34	83.20	78.88	111.11	242.38	
		Solvent	113.17	82.92	79.40	114.12	249.36	
	Acetone and methyl alcohol . . . . .	0°	10	104.18	134.61	177.56	211.62	188.91
			Solvent	110.72	153.92	193.16	230.54	198.24
25°		10	157.37	185.86	202.74	218.99	242.38	
		Solvent	164.34	195.49	213.92	235.12	249.36	
Acetone and ethyl alcohol . . . . .		0°	10	44.71	76.80	126.04	186.81	188.91
			Solvent	47.44	86.53	141.24	204.07	198.24
	25°	10	79.28	128.07	165.92	214.45	242.38	
		Solvent	83.54	131.29	185.98	224.57	249.36	
	Methyl alcohol and ethyl alcohol . . . . .	0°	10	44.71	58.58	74.56	94.46	104.18
			Solvent	47.44	61.84	77.45	99.68	110.72
25°		10	79.28	101.10	120.91	149.56	157.37	
		Solvent	83.54	105.27	126.51	147.24	164.34	
			Solvent	87.36	105.48	124.86	147.29	164.36

TABLE 86. — Comparison of temperature coefficients of fluidity of potassium sulphocyanate from 0° to 25°.

Mixture.	$v$	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Methyl alcohol and water . . . . .	10	0.0387	0.0588	0.0565	0.0425	0.0204
	Solvent	.0398	.0607	.0571	.0419	.0194
Ethyl alcohol and water . . . . .	10	.0387	.0804	.0856	.0608	.0309
	Solvent	.0398	.0837	.0892	.0633	.0337
Acetone and water . . . . .	10	.0387	.0548	.0548	.0372	.0113
	Solvent	.0398	.0552	.0552	.0377	.0107
Acetone and methyl alcohol	10	.0204	.0152	.00567	.00139	.0113
	Solvent	.0194	.0111	.00604	.00175	.0107
Acetone and ethyl alcohol . . . . .	10	.0309	.0267	.0127	.00592	.0113
	Solvent	.0337	.0231	.0131	.00462	.0107
Methyl alcohol and ethyl alcohol . . . . .	10	.0309	.0290	.0249	.0195	.0204
	Solvent	.0337	.0282	.0229	.0191	.0194

Tables 84 and 85 (fig. 98) show that potassium sulphocyanate, in mixtures of methyl alcohol and water, exhibits a marked minimum in fluidity in the 50 per cent mixture at 25° and at 0°, although in the latter case there is only a slight difference between the values in the 25 per cent and the 50 per cent mixtures. *It is of especial importance to note here that potassium sulphocyanate shows a marked negative viscosity (or positive fluidity) in water, and that the viscosity values do not become positive until a mixture about midway between*



Curve I, fluidities of mixture of methyl alcohol and water at 0°.  
 Curve II, fluidities of N/10 potassium sulphocyanate in mixtures of methyl alcohol and water at 0°.  
 Curve III, fluidities of the above solvent mixtures at 25°.  
 Curve IV, fluidities of N/10 potassium sulphocyanate in the above solvent mixtures at 25°.

FIG. 98.

the 50 per cent and 75 per cent mixtures is reached. In other words, N/10 solution of potassium sulphocyanate in water is much less viscous (or has a much greater fluidity) than pure water itself. On the other hand, a N/20 solution of potassium sulphocyanate in methyl alcohol has a greater viscosity (or smaller fluidity) than the pure solvent itself. These two effects become equal, and we have the viscosity (or fluidity) of the N/10 solution and the pure solvent equal in a mixture intermediate between the 50 per cent and 75 per cent mixtures. The normal or general action of a salt, when dissolved in water, is to increase the viscosity. Cases of negative viscosity have been noted by other workers, and this subject will be discussed later in this memoir. It should be noted that the difference in viscosity between the solution and the pure solvent is greater in methyl alcohol than it is in water, or any of the mixtures. The temperature coefficients of fluidity are greater in the pure solvents than in the solutions, in the 0 per cent, 25 per cent, and 50 per cent mixtures; and *vice versa* in the 75 per cent and 100 per cent mixtures, and

the temperature coefficients of fluidity themselves are greatest in the 25 per cent mixture.

Tables 84, 85, and 86 (fig. 99) show that potassium sulphocyanate, in mixtures of ethyl alcohol and water, exhibits a decided minimum in fluidity in the 50 per cent mixture. Here, also, there is the negative viscosity coefficient in the aqueous mixtures, up to a mixture intermediate between the 50 per cent and 75 per cent mixtures; from this point on it is positive. The difference in viscosity between the solutions and pure solvent is much greater in the pure ethyl alcohol than it is in pure water; and it will also be noted that the difference between the viscosity of the solution and the pure solvent, in the case of ethyl alcohol, is greater at 25° than at 0°. A study of the temperature coefficients of fluidity shows that in all the mixtures they are greater

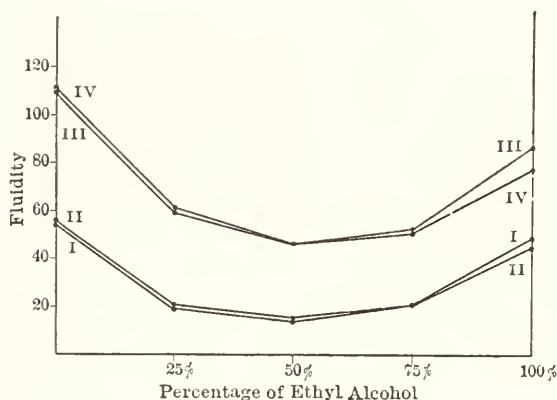


FIG. 99.

Curve I, fluidities of mixtures of ethyl alcohol and water at 0°.

Curve II, fluidities of N/10 potassium sulphocyanate in mixtures of ethyl alcohol and water at 0°.

Curve III, fluidities of the above solvent mixtures at 25°.

Curve IV, fluidities of N/10 potassium sulphocyanate in the above solvent mixtures at 25°.

for the pure solvent than they are for the solution. The temperature coefficients of fluidity are greatest in the 50 per cent mixture.

The temperature coefficients of fluidity decrease with increase in dilution in the 0 per cent, 25 per cent, and 100 per cent mixtures, and increase with increase in dilution in the 50 per cent and 75 per cent mixtures, which are the mixtures in which the maximum fluidity is shown.

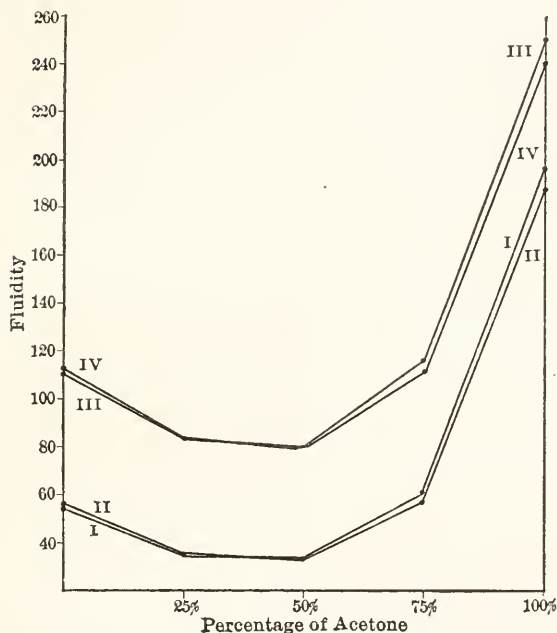
Tables 84, 85, and 86 (fig. 100) show that potassium sulphocyanate, in mixtures of acetone and water, exhibits a minimum in the fluidity curves in the 50 per cent mixtures at both 0° and 25°. Here, again, we have the negative viscosity coefficient in the aqueous solutions and in the 25 per cent mixtures. This negative coefficient becomes zero at some point intermediate between the 25 per cent and the 50 per cent mixtures; and is positive from that point on throughout the remaining mixtures. We must also call attention to the fact that the increase in viscosity with increase in dilution is



greater in acetone than it is in water, and that the viscosity of acetone is very much less than that of water.

The temperature coefficients of fluidity increase in all the mixtures, with the exception of the 100 per cent mixtures, with increase in dilution; and the largest coefficients are in the 25 per cent and 50 per cent mixtures; the values in these two cases being identical to the fourth decimal place.

Tables 84, 85, and 86 (fig. 101) show that potassium sulphocyanate, in



Curve I, fluidities of mixtures of acetone and water at 0°.  
 Curve II, fluidities of N/10 potassium sulphocyanate in mixtures of acetone and water at 0°.  
 Curve III, fluidities of the above solvent mixtures at 25°.  
 Curve IV, fluidities of potassium sulphocyanate in the above solvent mixtures at 25°.

FIG. 100.

mixtures of acetone and methyl alcohol, exhibits a marked maximum which disappeared at 25°. The curves at 25°, however, show an increase in the fluidity at 0°, in the 75 per cent mixtures, but that this maximum has values above the average values for the two solvents. It is to be noted also, that although the increase in fluidity with increase in dilution is nearly the same in acetone and methyl alcohol, yet this increase is very much greater in the mixtures, and especially in the 50 per cent and 75 per cent mixtures.

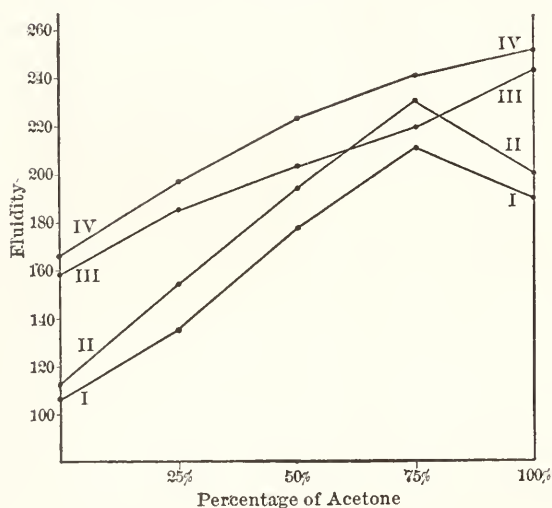
Tables 84, 85, and 86 (fig. 102) show that tenth-normal potassium sulphocyanate, in mixtures of acetone and ethyl alcohol, exhibits a maximum in fluidity in the 75 per cent mixture at 0°. The pure solvent at 0°, and the solutions and solvent at 25° do not exhibit this maximum, although they do

show an increase above the values calculated on the basis of averages. It is to be noted also that the increase in fluidity with increase in dilution is greatest in the 50 per cent and 75 per cent mixtures.

The temperature coefficients of fluidity increase with increase in dilution in the 0 per cent and 50 per cent mixtures; but decrease with increasing dilution in the 25 per cent, 75 per cent, and 100 per cent mixtures. The largest values are found in the 0 per cent solutions.

Tables 84, 85, and 86 (fig. 103) show that potassium sulphocyanate, in mixtures of methyl alcohol and ethyl alcohol, exhibits an increase in fluidity above the average values in the 50 per cent and 75 per cent mixtures.

The temperature coefficients of fluidity decrease with increase in dilution



Curve I, fluidities of N/10 potassium sulphocyanate in mixtures of acetone and methyl alcohol at 0°.

Curve II, fluidities of mixtures of acetone and methyl alcohol at 0°.

Curve III, fluidities of N/10 potassium sulphocyanate in the above mixtures at 25°.

Curve IV, fluidities of the above solvent mixtures at 25°.

FIG. 101.

in every case, except the 0 per cent mixture, the maximum value being in the 0 per cent mixture.

Table 85 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of methyl alcohol and water, increase with increase in dilution of the solutions in the 0 per cent, 25 per cent, and 50 per cent mixtures; and decrease with increase in dilution in the 75 per cent and 100 per cent mixtures. The temperature coefficients of conductivity of copper chloride in these mixtures increase with increasing dilution in every case, except the 100 per cent mixture, where the opposite condition holds. The temperature coefficients of conductivity of potassium sulphocyanate increase with increase in dilution in all of the solvents. The temperature coefficients of fluidity are largest in the 25 per cent mixture, and such is the case also for

the temperature coefficients of conductivity of both copper chloride and potassium sulphocyanate.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of ethyl alcohol and water, increase in all cases with increase in dilution. The same is true of the temperature coefficients of conductivity of both copper chloride and potassium sulphocyanate. The temperature coefficients of fluidity are largest in the 50 per cent mixtures,

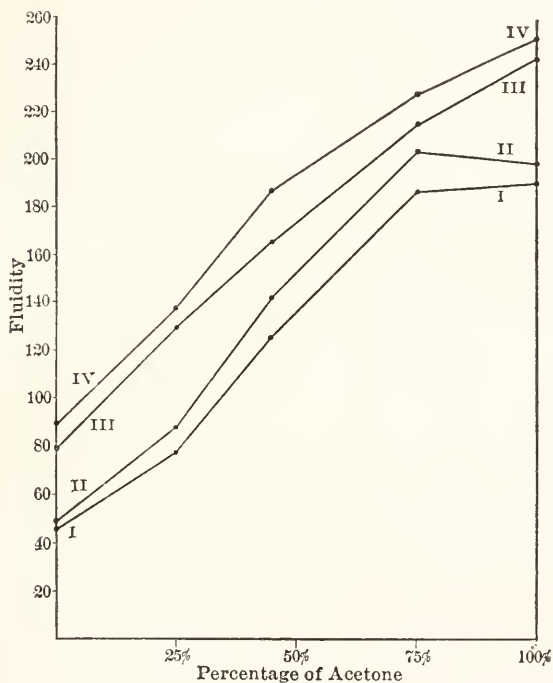


FIG. 102.

Curve I, fluidities of N/10 potassium sulphocyanate in mixtures of acetone and ethyl alcohol at 0°.  
 Curve II, fluidities of mixtures of acetone and ethyl alcohol at 0°.  
 Curve III, fluidities of N/10 potassium sulphocyanate in the above mixtures at 25°.  
 Curve IV, fluidities of the above solvent mixtures at 25°.

and the same is true of the temperature coefficients of conductivity of both the above-mentioned salts.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of acetone and water, increase with increasing dilution, with the exception of the solutions in the pure acetone. The maximum values for these temperature coefficients are found in the 25 per cent and 50 per cent mixtures. The temperature coefficients of conductivity of potassium sulphocyanate, in these mixtures, increase with increase in dilution, the maximum values being in the 50 per cent mixture.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of acetone and methyl alcohol, decrease with

increase in dilution in the 0 per cent, 25 per cent, and 100 per cent mixtures, and *vice versa* in the 50 per cent and 75 per cent mixtures. The maximum values are in methyl alcohol. The temperature coefficients of conductivity of potassium sulphocyanate, on the other hand, increase with increase in dilution in every case, and the maximum values are in methyl alcohol.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of acetone and ethyl alcohol, increase with increase

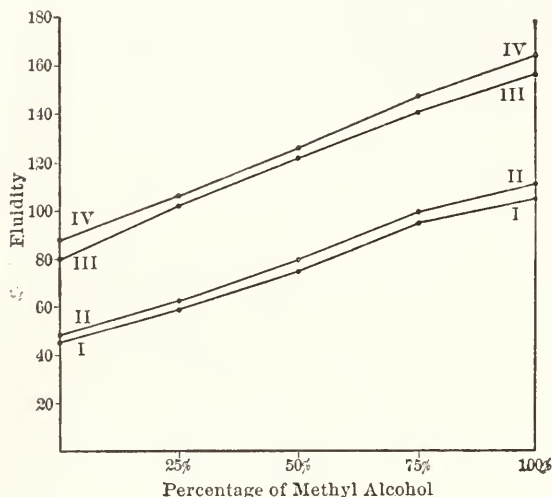


FIG. 103.

Curve I, fluidities of N/10 potassium sulphocyanate in mixtures of methyl alcohol and ethyl alcohol at 0°.

Curve II, fluidities of mixtures of methyl alcohol and ethyl alcohol at 0°.

Curve III, fluidities of N/10 potassium sulphocyanate in the above mixtures at 25°.

Curve IV, fluidities of the above mixed solvents at 25°.

in dilution in the 0 per cent and 50 per cent mixtures, but decrease in the 25 per cent, 75 per cent, and 100 per cent mixtures. The maximum values are in the 0 per cent mixture. The temperature coefficients of conductivity of potassium sulphocyanate in these mixtures increase in every case with increase in dilution. The maximum values are in the 0 per cent mixture.

Table 87 shows that the temperature coefficients of conductivity of copper chloride increase with increase in dilution in all cases, except the 100 per cent mixture, the maximum values being in the 0 per cent mixture.

The corresponding temperature coefficients for potassium sulphocyanate increase with increasing dilution in all cases, and the maximum values are in the 0 per cent mixture.

#### A SUMMARY OF THE FACTS ESTABLISHED.

(1) A minimum in conductivity has been noted in the following cases: Potassium sulphocyanate in 50 per cent methyl alcohol and water at 0°. This shifts to the 75 per cent mixture at 25°. Also in 50 per cent acetone

and water at 0° and 25°, with the single exception of the N/10 solution at 25°. Likewise, in the 50 per cent and 75 per cent mixtures of ethyl alcohol and water, with the exception of the N/10 solution at 0°. At 25° the N/800 and N/1600 solutions show minimum values, these occurring in the 75 per cent mixture.

TABLE 87. — Comparison of the temperature coefficients of conductivity and fluidity.

		$v$	Dissolved substance.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	
In mixtures of methyl alcohol and water.	Fluidity . .	{	10	KCNS	0.0387	0.0588	0.0565	0.0425	0.0204
			Solvent	.....	.0398	.0607	.0571	.0419	.0194
	Conductivity	{	10	CuCl <sub>2</sub>	.0329	.0421	.0372	.0237	.00984
			1600	CuCl <sub>2</sub>	.0371	.0475	.0437	.0318	.00523
			10	KCNS	.0316	.0410	.0400	.0304	.0154
			1600	KCNS	.0325	.0419	.0429	.0352	.0169
In mixtures of ethyl alcohol and water.	Fluidity . .	{	10	KCNS	.0387	.0804	.0856	.0608	.0309
			Solvent	.....	.0398	.0837	.0892	.0633	.0337
	Conductivity	{	10	CuCl <sub>2</sub>	.0329	.0543	.0556	.0360	.0153
			1600	CuCl <sub>2</sub>	.0371	.0635	.0683	.0432	.0235
			10	KCNS	.0316	.0518	.0590	.0449	.0224
			1600	KCNS	.0325	.0600	.0636	.0490	.0268
In mixtures of acetone and water.	Fluidity . .	{	10	KCNS	.0387	.0548	.0548	.0372	.0113
			Solvent	.....	.0398	.0552	.0552	.0337	.0107
	Conductivity	{	10	CuCl <sub>2</sub>	.0329	...	...	...	...
			1600	CuCl <sub>2</sub>	.0371	...	...	...	...
			10	KCNS	.0316	.0398	.0402	.0283	.00481
			1600	KCNS	.0325	.0404	.0432	.0312	.00815
In mixtures of acetone and methyl alcohol.	Fluidity . .	{	10	KCNS	.0204	.0152	.00567	.00139	.0113
			Solvent	.....	.0194	.0111	.00604	.00175	.0107
	Conductivity	{	10	CuCl <sub>2</sub>	.00984	...	.....	.....	.....
			1600	CuCl <sub>2</sub>	.00823	...	.....	.....	.....
			10	KCNS	.0154	.0138	.0123	.00971	.00481
			1600	KCNS	.0169	.0157	.0140	.01176	.00815
In mixtures of acetone and ethyl alcohol.	Fluidity . .	{	10	KCNS	.0309	.0267	.0127	.00592	.0113
			Solvent	.....	.0337	.0231	.0131	.00462	.0107
	Conductivity	{	10	CuCl <sub>2</sub>	.0153	...	.....	.....	.....
			1600	CuCl <sub>2</sub>	.0235	...	.....	.....	.....
			10	KCNS	.0224	.0172	.0126	.00868	.00481
			1600	KCNS	.0268	.0201	.0175	.01237	.00815
In mixtures of methyl alcohol and ethyl alcohol.	Fluidity . .	{	10	KCNS	.0309	.0290	.0249	.0195	.0204
			Solvent	.....	.0337	.0282	.0229	.0191	.0194
	Conductivity	{	10	CuCl <sub>2</sub>	.0153	.00992	.00901	.00853	.00984
			1600	CuCl <sub>2</sub>	.0235	.01831	.01620	.01260	.00823
			10	KCNS	.0224	.0204	.0183	.0166	.0134
			1600	KCNS	.0268	.0237	.0209	.0181	.0169

(2) A decided fall below the average values for the two pure solvents has been noted in the following mixtures: (a) Copper chloride in methyl alcohol and water, the fall being most pronounced in the 50 per cent mixture; in ethyl alcohol and water in the 25 per cent and 50 per cent mixtures; in methyl alcohol and ethyl alcohol in the 25 and 50 per cent mixtures. (b) Potassium sulphocyanate in mixtures of methyl alcohol and ethyl alcohol, the concentrations being N/400, N/800, and N/1600; in mixtures of acetone and methyl alcohol, and in the mixtures of acetone and ethyl alcohol.

(3) It has been noted that in every case where there is not an actual minimum shown by the curves, but simply the falling below the average values, there is a wide difference between the conductivity values in the two unmixed or pure solvents. It is quite evident that this difference must play a large

part in determining whether there will be an actual minimum in the curves or not; and we wish especially to point out the fact that although an actual minimum is not shown in every case, yet we have virtually a minimum in the conductivity values whenever the pure solvents are mixed; and that this minimum occurs in the 50 per cent and 75 per cent mixtures. There are only a very few exceptions to the above statement, and these exceptions will be pointed out in paragraph 4.

(4) A maximum in conductivity has been noted in the following cases: Potassium sulphocyanate in 75 per cent acetone and methyl alcohol in the N/10, N/50, and N/100 solutions at 0°, and in the N/10, N/50, N/100, and N/200 solutions at 25°. In acetone and ethyl alcohol the N/10 solutions, in the 75 per cent mixture, show a pronounced maximum; and a decided tendency towards a maximum is shown by the N/50, N/100, and N/200 solutions.

(5) It has been noted that there is a marked difference not only between the actual numerical values for molecular conductivity, but also between the corresponding increase in the values with increase in dilution, for copper chloride (a ternary electrolyte) and potassium sulphocyanate (a binary electrolyte) in a given pure solvent. In pure water, for example, the conductivity of copper chloride at 25° increases from 162.6, in the N/10 solution, to 249.7, in the N/1600 solution, while the conductivity of potassium sulphocyanate under the same conditions increases from 112.7 to 131.6.

In other words, the conductivity values for copper chloride in water are much greater than the corresponding values for potassium sulphocyanate.

In pure methyl alcohol the conductivity of copper chloride at 25° increases from 17.98 to 72.64, while the conductivity of potassium sulphocyanate under the same conditions increases from 64.81 to 102.41. Thus we see that although the conductivity of copper chloride, in water, is much greater than the conductivity of potassium sulphocyanate in aqueous solution, yet in methyl alcohol exactly the reverse is true, *i. e.*, the conductivity of copper chloride in methyl alcohol is much less than that of potassium sulphocyanate under the same conditions.

In pure ethyl alcohol the conductivity of copper chloride at 25° increases from 4.88 to 25.24. Potassium sulphocyanate, on the other hand, under the same conditions, increases from 22.97 to 42.73.

Data similar to those just referred to have been obtained by other workers in this field. From the work of Jones and McMaster<sup>1</sup> we see that lithium bromide (a binary electrolyte) shows an increase in conductivity from the N/10 solution to the N/1600 solution in water, of from 86.09 to 106.23.

Cobalt chloride (a ternary electrolyte) shows an increase of from 156.36 to 221.50, over the same range in dilution.

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<sup>1</sup> Amer. Chem. Journ., **36**, 335-381 (1906).

In methyl alcohol they found that lithium bromide increases from 50.21 to 83.64, and cobalt chloride from 41.78 to 133.33 for the same increase in dilution.

In ethyl alcohol lithium bromide increases from 17.22 to 33.36; and cobalt chloride from 7.64 to 33.59, between the N/10 and the N/1600 solutions.

In acetone lithium bromide increases from 110.82 to 85.90 over the above range in dilution, and cobalt chloride increases from 9.47 in the N/100 solution to 10.45 in the N/1600 solution.

Jones and Bingham<sup>1</sup> obtained the following data with lithium nitrate, potassium iodide, and calcium nitrate: Lithium nitrate in water, between the N/10 and N/1600 solutions increases from 83.9 to 102.8; potassium iodide in water between the N/200 and N/1600 solutions increases from 136.3 to 140.7; calcium nitrate in water between the N/10 and N/1600 solutions increases from 165.5 to 249.8. Here, again, we observe that the ternary electrolytes show a much greater conductivity in aqueous solutions than do the binary electrolytes.

Lithium nitrate in methyl alcohol, between the N/10 and N/1600 solutions increases from 51.31 to 86.7; potassium iodide in methyl alcohol between the N/200 and N/1600 solutions increases from 91.4 to 103.3; calcium nitrate in methyl alcohol between the N/10 and the N/1600 solutions increases from 17.17 to 35.4; potassium iodide in ethyl alcohol between the N/200 and N/1600 solutions increases from 34.6 to 42.8.

Calcium nitrate in ethyl alcohol between the N/10 and the N/1600 solutions increases from 7.86 to 33.3; lithium nitrate in acetone under the same conditions increases from 10.87 to 59.8; potassium iodide in acetone between the N/200 and the N/1600 solutions increases from 118.0 to 141.1; and calcium nitrate in acetone between the N/210 and the N/1600 solutions increases from 5.67 to 12.62.

(6) The temperature coefficients of conductivity increase with increase in dilution, with one exception. This exception is copper chloride in methyl alcohol. The increase is not regular, but it is quite decided when the difference in the values for the N/10 and the N/1600 solutions is considered.

(7) The temperature coefficients of conductivity are always a maximum in the mixtures of water with the alcohols or acetone, and are never a maximum in the mixtures of the alcohols with each other or with acetone.

The individual facts upon which the above statement is based are as follows: Copper chloride in 25 per cent methyl alcohol and water; in 50 per cent ethyl alcohol and water; potassium sulphocyanate in 25 per cent and 50 per cent mixtures of methyl alcohol and water, and in 50 per cent acetone and water, and in 50 per cent ethyl alcohol and water.

The data obtained by Jones and McMaster<sup>2</sup> show that this is also true for

<sup>1</sup> Amer. Chem. Journ., **34**, 497-534 (1905).

<sup>2</sup> Loc. cit.

lithium bromide in 25 per cent methyl alcohol and water, in 50 per cent ethyl alcohol and water, and in 50 per cent acetone and water. It is also true for cobalt chloride, in 25 per cent methyl alcohol and water, in 50 per cent ethyl alcohol and water, and in 75 per cent acetone and water.

By reference to the work of Jones and Bingham <sup>1</sup> we see that this is likewise true for lithium nitrate in 25 per cent acetone and water, for potassium iodide in 50 per cent acetone and water, and for calcium nitrate in 25 per cent and 50 per cent acetone and water.

(8) The molecular conductivities of potassium sulphocyanate in acetone, as compared with the corresponding conductivities in water, bring out some important facts. The conductivity values in the N/10 solutions are usually much smaller in acetone than they are in water, but with increase in dilution they become very much larger in acetone than they do in water. The same thing is seen to be true when the conductivity of the acetone solutions is compared with the solutions in the alcohols, but to a smaller degree. The values become greater in acetone than they do in either of the alcohols.

(9) A marked minimum in fluidity has been noted in the following cases: 50 per cent methyl alcohol and water at 0° and 25°, 50 per cent ethyl alcohol and water, 50 per cent acetone and water.

(10) A maximum in fluidity has been noted in the following cases: In 75 per cent acetone and methyl alcohol at 0°. Although this maximum has disappeared at 25°, yet there is a decided increase of the values in the mixture above the average values; in N/10 potassium sulphocyanate in 75 per cent acetone and ethyl alcohol at 0°. The pure solvent does not show the maximum at 0°, and the maximum has entirely disappeared at 25° in both the solution and the solvent, but nevertheless there is an increase above the average values in each case in the 75 per cent mixture. This increase above the average values is also shown by the mixtures of methyl alcohol and ethyl alcohol.

(11) A marked negative viscosity coefficient is shown by potassium sulphocyanate in aqueous solution. In the other pure solvents, methyl alcohol, ethyl alcohol, and acetone, potassium sulphocyanate gives a positive viscosity coefficient, and in mixtures of the other solvents with water the viscosity coefficient becomes zero in the following mixtures: At a point about midway between the 50 per cent and 75 per cent mixtures of methyl alcohol and water; and in the same mixtures of ethyl alcohol and water, and between the 25 per cent and 50 per cent mixtures of acetone and water.

(12) The temperature coefficients of fluidity are a maximum in the mixtures of the other solvents with water in the 25 and 50 per cent mixtures, and in no case are they a maximum in the mixtures of the alcohols and acetone with one another.

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<sup>1</sup> Loc. cit.



## DISCUSSION OF RESULTS.

It would be desirable for some reasons to discuss the facts brought out by our study of conductivity in one section, and the results of the work on fluidity in a separate section; but on account of the close relations between conductivity and fluidity it seems best to take up the discussion in such a manner as to bring out more clearly the bearing of these relations upon one another.

An explanation of the minimum in molecular conductivity has been offered by Jones and Lindsay,<sup>1</sup> and, as has already been pointed out in the introductory section of this paper, this has been experimentally substantiated by the work of Jones and Murray.<sup>1</sup> This explanation was, however, applied only to the cases where an actual minimum occurs, but, as we have already pointed out, there are fully as many cases in which the curves show simply a falling below the values as calculated from the rule of averages. We have shown that in these cases we have what we may call a *virtual minimum*, and we extend the hypothesis of Jones and Lindsay to these cases also, since it bears as we believe on both the actual minima and the virtual minima. Since these two conditions cover by far the greater majority of the conductivity results that have been obtained up to the present in mixed solvents, it appears that the hypothesis of Jones and Lindsay when applied to the problem of conductivity in mixed solvents is perfectly general.

A further proof of this explanation has been brought out by our study of fluidity. A marked minimum in fluidity occurs in the 50 per cent mixtures of water and methyl alcohol, water and ethyl alcohol, and water and acetone. It is in these same mixtures that the minimum in conductivity occurs.

F. H. Getman,<sup>2</sup> in discussing the maximum viscosity (or minimum fluidity, which occurs when the alcohols and water are mixed, drew the conclusion that if the association of one liquid is diminished by the presence of another associated liquid, then the viscosity of a 50 per cent mixture of these liquids should be less than the viscosity as calculated from the rule of averages. This conclusion, as we shall see, is erroneous. The work of Thorpe and Rodger<sup>3</sup> has clearly shown that viscosity may be taken as the sum of the forces in play between the molecules. Therefore, when two associated liquids are mixed, if they mutually decrease the association of one another, the total number of molecules in a given volume of the mixtures is increased, and consequently

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<sup>1</sup> Loc. cit.    <sup>2</sup> Journ. chim. Phys., **4**, 403 (1906).    <sup>3</sup> Phil. Trans., **185A**, 307 (1894).

the total surface of the molecules of the solvents is increased, *i. e.*, the *total frictional surface is increased*, and *an increase in viscosity results*. The point at which the viscosity of the mixed solvents becomes a maximum, is, then, the point at which the effect above mentioned of the pure solvents on each other is the greatest. Thus we see that at the point where we find the maximum in viscosity we have the greatest number of simple molecules of the two solvents present.

According to this view of the cause of the fluidity minimum (or viscosity maximum), the reason for the minimum in the conductivity curve follows at once. Since the association of the solvents is a minimum at the point of minimum fluidity, the dissociating power of the solvents is also at a minimum, and the minimum in conductivity is a natural consequence.

As has already been stated, it is at the minimum points of conductivity that we have the phenomenon of a very small increase in molecular conductivity with increase in dilution, as is shown by the conductivity curves for the different dilutions approaching one another as they approach the minimum. This also is a natural consequence of our theory. The association of the solvents being a minimum at these points, as has already been shown, their dissociating power is also a minimum, and, consequently, an increase in the amount of the solvent present has little influence on the dissociation of the dissolved salt. To elaborate this a little more fully, let us suppose that the salt were dissolved in a solvent which had no dissociating power; then no matter how much of the solvent were present, the dissociation of the salt and, consequently, the molecular conductivity of the solution would remain zero. If, now, a solvent is used which has very small dissociating power, it is evident that comparatively large amounts of it would be required to produce any very appreciable effect upon the dissociation of the dissolved salt.

In a few cases a maximum in conductivity was observed. These cases occur in certain of the mixtures of acetone with the alcohols. Similar examples, and in these same solvents, were first observed by Jones and Bingham,<sup>1</sup> who suggested the explanation that these maxima are due either to an increase in the number of ions present, or to a diminution in the size of the ionic spheres, making possible a more rapid movement of the ions. As has been pointed out, their final conclusion is that the latter explanation, *i. e.*, a diminution in the size of the ionic spheres, is the more probable. The question, however, arises: Why does this change in the size of the ionic spheres take place?

The experimental data, obtained up to the present, are not sufficient to justify a final answer to this question. We offer the following suggestion, however, as probable: The *increase in fluidity*, in view of what has already been said with regard to the cause of maxima and minima in the fluidity

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<sup>1</sup> Loc. cit.

curves, is *probably due to an increase in the molecular aggregation of the solvent*. This increase is not necessarily caused by an increase in the association of either of the pure solvents. Indeed, the association of the pure solvents is in all probability less in the mixtures. The increase in molecular aggregation above referred to may simply be due to a molecular combination of the unassociated parts of the pure solvents. The view that is now generally held with regard to chemical combination is that such combination usually takes place between the ions and not between the molecules. We may, in a sense, regard a molecule that is broken down into its ions as in a state of diminished atomic aggregation, just as we regard the diminution in association, when two pure solvents are mixed, as a state of diminished molecular aggregation. The ions, to be sure, are in a different physical condition from the undissociated molecule, in that they carry equal and opposite electrical charges; and we have no experimental reason whatsoever for supposing that the unassociated portions of the solvent molecules, in the mixed solvents, are in the same condition. It is, however, the difference in energy relations between the ions that is at the basis of our present views of chemical combination. Reasoning from analogy, it is not unthinkable, to say the least, that a similar, although not identical difference in energy relations is the cause of molecular aggregation or association. If such an energy relation as has been referred to does exist, then we have an explanation of the formation of complex molecules, such as hydrates, double salts, etc. If the above reasoning is correct, the explanation of the fluidity maximum is simple. According to Ramsay and Shields <sup>1</sup> the molecular complexity of the four solvents is as follows:

Substance.	Molecular complexity between 0° and 25°.
Water . . . . .	(H <sub>2</sub> O) <sub>4</sub> .
Methyl alcohol . . . . .	(CH <sub>3</sub> OH) <sub>3.4</sub>
Ethyl alcohol . . . . .	(C <sub>2</sub> H <sub>5</sub> OH) <sub>2.7</sub>
Acetone . . . . .	(CH <sub>3</sub> COCH <sub>3</sub> ) <sub>1.26</sub>

From these data we see that the molecules of methyl alcohol and the molecules of ethyl alcohol are much more complex than the molecules of acetone. For the sake of simplicity we shall limit our discussion to the case of mixtures of acetone and methyl alcohol. The maximum in fluidity occurs in the 75 per cent mixture of the two solvents. We should expect the effect of the acetone upon the methyl alcohol to be greatest in about this mixture, because of the relatively large mass of the acetone present; and, consequently, in such a mixture we should have the largest number of unassociated molecules of methyl alcohol. This is shown to be the case by reference to the temperature

<sup>1</sup> Ztschr. phys. Chem., **12**, 433 (1893).

coefficients of fluidity of the pure solvents, which are a minimum in the 75 per cent mixture. The methyl alcohol, being much more associated than the pure acetone, a small mass of it would cause a proportionally greater decrease in the association of the acetone, and in about the 75 per cent mixture we should expect to find the condition for molecular combination of these two solvents most favorable. The complex molecule thus formed explains the fluidity maximum, in terms of the view of viscosity and fluidity maxima and minima that we have already suggested. Since the fluidity of the solvent has become much greater, the ionic velocity is increased.

Thus we conclude that the maximum in conductivity is dependent upon two factors: *The change in the size of ionic spheres and the change in the fluidity of the solvent.*

Reference to the work of J. J. Thompson,<sup>1</sup> Brühl,<sup>2</sup> Nernst,<sup>3</sup> Ciamician,<sup>4</sup> Dutoit and Aston,<sup>5</sup> Ramsay and Shields,<sup>6</sup> Crompton,<sup>7</sup> and Donnan,<sup>8</sup> shows that the prevailing idea concerning the action of dissociating solvents upon dissolved electrolytes is that the dissociating action of the solvent is mainly a function of the dielectric constant and the degree of association of the solvent. We wish, however, to call attention again to the fact that the dissociating action of the solvent is also dependent largely upon the nature of the dissolved electrolyte. We have already seen that the conductivity of copper chloride in water is much greater than the corresponding conductivity of potassium sulphocyanate in water. Now if the dissociating action of all solvents were solely a function of the properties of the solvent, we should expect the conductivity of copper chloride in any other solvent to be greater than the corresponding conductivity of potassium sulphocyanate in that solvent. But such is not the case, since we find that in methyl alcohol, for example, the conditions are exactly the reverse of what they are in water, and, further, that potassium sulphocyanate has a much greater conductivity in methyl alcohol than copper chloride has under the same conditions.

A number of other similar cases have been mentioned in the "General summary of facts established" in this section. These facts show conclusively that the nature of the dissolved salt also plays a large part in determining what the dissociating action of any given solvent will be. The probable explanation of the marked difference in the action of dissociating solvents towards binary and ternary electrolytes is, in the case of water and methyl alcohol for example, as follows: Water, being a highly associated solvent, has the power of breaking down the ternary electrolytes into the simplest ions, each molecule of the ternary electrolyte yielding three ions.

<sup>1</sup> Phil. Mag., **36**, 320 (1893).

<sup>2</sup> Ztschr. phys. Chem., **13**, 531 (1894).

<sup>3</sup> Ibid., **18**, 514 (1895); **27**, 319 (1898); **30**, 1 (1899).

<sup>4</sup> Ibid., **6**, 403 (1890).

<sup>5</sup> Compt. rend., **125**, 240 (1897).

<sup>6</sup> Ztschr. phys. Chem., **12**, 433 (1893).

<sup>7</sup> Journ. Chem. Soc., **71**, 925.

<sup>8</sup> Phil. Mag., (6) **15**, 305.

Methyl alcohol, on the other hand, being less associated than water, probably has the power to break down the ternary electrolytes into only two ions, whereas the binary electrolytes are broken down into ions in both the water and the alcohol. The increase in the temperature coefficients with increase in dilution in aqueous solutions has been explained by Jones,<sup>1</sup> and the same explanation doubtless holds for the increase in the temperature coefficients with increase in dilution in the mixed solvents. In the mixed solvents we probably have a sphere around the ions, which is composed of molecules of both the pure solvents. The fact that such solvates are formed in other solvents than water has been established by the work of Jones and McMaster.<sup>2</sup>

The temperature coefficients of conductivity are a maximum in the 25 per cent and 50 per cent mixtures of water and the other solvents, as has already been pointed out. At first glance this seems to be a remarkable fact, in view of the large amount of experimental evidence that has been furnished by Jones and his co-workers upon the hydrate theory as proposed by Jones. There seems to be but one explanation, viz, that in these particular mixtures the most complex solvates are formed. These complex solvates change in complexity more rapidly with change in temperature than the less complex solvates, and, consequently, the temperature coefficients are a maximum. The question, however, naturally arises, Why are the solvates more complex in one mixture than in another? It will be observed that the maximum temperature coefficients of conductivity in mixtures of methyl alcohol and water are found, as a rule, in the 25 per cent mixtures; yet they also occur in some cases in the 50 per cent mixtures. The maximum values of these temperature coefficients of conductivity in mixtures of ethyl alcohol and water occur most frequently in the 50 per cent mixture, although in some cases they are found in the 25 per cent mixture.

The maximum values of the temperature coefficients of conductivity in mixtures of acetone and water are mainly in the 50 per cent mixture, a few values occurring in the 75 per cent mixture. These facts are significant when considered in the light of the degree of association of the solvents involved, as shown by the table previously given.

Acetone being the least associated of this group of solvents, we should expect its greatest action in diminishing the association of water to occur in about the 75 per cent mixture, where the mass of the acetone is very great. We should expect this effect to manifest itself in the smaller percentage mixtures, when mixtures with water, of more highly associated solvents than acetone, are considered. A glance at the fluidity values shows that although mixtures of methyl alcohol and water show a minimum in the 50 per cent

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<sup>1</sup> Amer. Chem. Journ., **35**, 445 (1906).

<sup>2</sup> Ibid., **35**, 316 (1906).

mixture, yet there is a much more pronounced tendency towards a minimum in the 25 per cent mixture than there is in the 75 per cent mixture. We see also that although the mixtures of ethyl alcohol and water show a minimum in the 50 per cent mixture, yet there is a more marked tendency towards a minimum in the 75 per cent mixture than there is in the 25 per cent mixture. The case of mixtures of acetone and water is not quite so clean cut, but here again the minimum in fluidity is in the 50 per cent mixture; and although the actual value of the fluidity in the 75 per cent mixture is greater than it is in the 25 per cent mixture, yet, when the very great difference between the fluidity of acetone and the fluidity of water is considered, it is readily seen that in this case also the tendency towards a minimum in fluidity is more marked in the 75 per cent mixture than it is in the 25 per cent mixture.

These facts show clearly that in about the 25 and 50 per cent mixtures of the other solvents with water we have the most favorable conditions for the formation of molecular aggregations, such as solvates, between the ions of the dissolved salt and the molecules of the solvents. In other words, we should have the greatest number of simple solvent molecules present in the mixtures above mentioned; and, as we have already pointed out in another connection, these are the conditions under which we can most reasonably expect the greatest combination between the solvent and the dissolved salt.

The fact that the molecular conductivities of potassium sulphocyanate in acetone are smaller than they are in water for the more concentrated solutions, but are much greater in acetone than they are in water for the more dilute solutions, might be due to several causes.

First, a much greater degree of dissociation, and a more rapid increase in dissociation with increase in dilution, in acetone than in water. This view, however, is untenable in view of the fact that acetone is very much less associated than water, and has a much smaller dielectric constant. Indeed, these facts lead us to the conclusion that potassium sulphocyanate is much less dissociated in acetone than it is in water.

Second, a much greater velocity of the ions in acetone than in water. That this is the probable explanation is shown by the following considerations: The fluidity of acetone is very much greater than the fluidity of water, and this, to be sure, is one of the factors that governs an increase in the ionic velocity; but a far more important factor becomes manifest from a study of the temperature coefficients of conductivity. It is a very significant fact that the temperature coefficients of conductivity in water are nearly ten times as great as the corresponding coefficients in acetone. This shows quite clearly that the solvates formed in the acetone solutions are very much less complex than those formed in the aqueous solutions. Since the ions in acetone have, as we have just seen, a much smaller atmosphere of solvent to

carry with them as they move through the solution than they have in the aqueous solutions, their velocity becomes much greater. These two factors both act in the same direction, *i. e.*, they both tend to increase the ionic velocity, and are quite sufficient to justify the conclusion that the molecular conductivities of potassium sulphocyanate are greater in acetone than they are in water, because of a very great increase in the velocity of the ions in the acetone solutions.

#### NEGATIVE VISCOSITY COEFFICIENTS.

It has been known for a number of years *that when certain salts are dissolved in water the resulting solutions have a smaller viscosity than the pure water*. Several theories have been proposed to explain this phenomenon. A brief but comprehensive outline of these theories has been given by Jones and Bingham,<sup>1</sup> and a mere reference to the literature will suffice in this connection. Euler<sup>2</sup> employed the "electrostriction theory" of Drude and Nernst<sup>3</sup> as a probable explanation of the negative viscosities; but it was later shown by Wagner<sup>4</sup> that this theory is incorrect, because the viscosity of a solvent may be lowered by the addition of certain non-electrolytes. Dunstan,<sup>5</sup> Blanchard,<sup>6</sup> Varenne and Godefroy,<sup>7</sup> Thorpe and Rodger, and Traube<sup>8</sup> all seem to attribute the abnormalities in viscosity to the presence of hydrates. The hydrate work of Jones and his co-workers has clearly shown that potassium chloride and similar salts are but little hydrated, even in dilute solutions; and since potassium chloride is one of the salts which produces a marked negative viscosity when dissolved in water, it is very difficult to see how hydrates could enter into the question of negative viscosity to any appreciable extent. Wagner<sup>9</sup> has made a study of the effect on the viscosity of water of about forty-five inorganic salts. From his data we find that the only salts which produce negative viscosity are the salts of caesium, rubidium, potassium, and thallium (in the thallos conditions), viz, caesium chloride, rubidium chloride, potassium chloride, potassium nitrate, and thallos nitrate. All potassium salts do not have this property of diminishing the viscosity of water. Potassium sulphate, potassium ferrocyanide, potassium ferricyanide, and potassium chromate, all give positive viscosity coefficients. But this is not at all surprising, since, as has already been mentioned, it was clearly shown that the viscosity of a salt solution is an additive function of the metallic and the non-metallic ions of the dissolved salt. In other words, the cations and anions seem to work counter to each other in some cases, such as potassium sul-

<sup>1</sup> Loc. cit.

<sup>2</sup> Ztschr. phys. Chem., **25**, 536 (1898).

<sup>3</sup> Ibid., **15**, 79 (1894).

<sup>4</sup> Ibid., **46**, 867 (1903).

<sup>5</sup> Ibid., **49**, 590 (1904).

<sup>6</sup> Journ. Amer. Chem. Soc., **26**, 1315 (1904).

<sup>7</sup> Compt. rend., **137**, 992 (1903); **138**, 990 (1904).

<sup>8</sup> Phil. Trans., **185A**, 307 (1894).

<sup>9</sup> Ztschr. phys. Chem., **5**, 31 (1890).

phate, where the  $\text{SO}_4$  ions tend to produce a positive viscosity coefficient to such a great extent as to overcome entirely the negative effect of the potassium ion; and the resultant action is the production of a positive viscosity coefficient by potassium sulphate when dissolved in water. The above facts show very clearly that there is some close connection between the physical properties of caesium, rubidium, and potassium and the negative viscosity phenomena. In discussing viscosity in general, Thorpe and Rodger<sup>1</sup> state that "Viscosity is, no doubt, the net result of at least two distinct causes. When a liquid flows, during the actual collision or contact of the molecules, a true, friction-like force will be called into play, opposing the movement. But in addition to this cause, even after the actual collision, molecular attractions will exercise a resistance to forces which tend to move one molecule past another."

Our study of viscosity has led us to the same conclusion as that arrived at by Thorpe and Rodger, viz, that viscosity phenomena are largely a function of the frictional surfaces of the ions, molecules, and molecular aggregates in any given solution. If now by any possible means the total frictional surface should be decreased, then the viscosity of the solution would also be decreased. Suppose that into a solvent containing molecules with comparatively small molecular volume we bring a salt which yields particles having relatively large atomic or ionic volumes. The larger particles of the dissolved substance would be distributed among the smaller molecules of the solvent, and these smaller molecules, instead of coming in contact with each other so frequently, would come in contact with the larger salt particles, and thus the total frictional surface involved would be decreased and, consequently, the viscosity of the solution would also be decreased. In other words, the effect of bringing those salts whose ions have large atomic volumes into pure water, would be the same as if some of the molecules of the water had combined into larger spheres, and thus caused a diminution in the total frictional surface. Since most salts do not produce such an effect on water, we must assume that their atomic volumes are too small, and that only the salts of those metals having very large atomic volumes could produce a diminution in the viscosity of water. The explanation proposed above for the negative viscosity phenomena can then be easily tested by a glance at the atomic volume curves of the elements. When this test is applied, we find that caesium, rubidium, and potassium stand at the *very maxima of the atomic volume curve, and that none of the other elements have anything like as large atomic volumes as the three elements just named*. Furthermore, if our hypothesis is correct, then *that ion which has the largest atomic volume should produce the greatest decrease in the viscosity of water, and the ion having the next smaller atomic volume should produce smaller decrease in the viscosity of water*. Here again we find that our theory

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<sup>1</sup> Loc. cit.



is in perfect accord with the facts, as far as they are recorded. According to the work of Wagner,<sup>1</sup> caesium chloride in normal solutions lowers the value of  $\eta^2$  from 1.0000 to 0.9775; rubidium chloride under the same conditions lowers the viscosity of water from 1.0000 to 0.9846; and potassium chloride in normal solution lowers the viscosity of water from 1.0000 to 0.9872. The atomic volume curve shows that caesium has the largest atomic volume (about 74), rubidium is next in order (about 57), and potassium has the smallest atomic volume (about 47) of this group of metals which produce the negative viscosity in water.

It is worth noting that the difference between the values of  $\eta$  for caesium chloride and rubidium chloride is much greater than the difference between rubidium chloride and potassium chloride. This is in keeping with the relative atomic volumes of the three elements. The difference between the atomic volumes of rubidium and caesium is much greater than the difference between the atomic volumes of rubidium and potassium.

If we extend the above conception to other cations with large atomic volumes, but with much smaller atomic volumes than the alkalis, we shall find that it holds satisfactorily. Take calcium, strontium, and barium, which, of all cations, have the next larger atomic volumes, and compare their chlorides with respect to the values of  $\eta$ ; we have, for normal solutions:

Calcium chloride . . . . .	$\eta$
Strontium chloride . . . . .	1.1563
Barium chloride . . . . .	1.1411
	1.1228

These values are all positive, as we should expect them to be, but their order is exactly the *reverse of the atomic volumes*, just as we should expect.

Chlorides with cations of smaller atomic volumes have values of  $\eta$  much larger than the above. This will be seen from the following table, where all the values of  $\eta$  refer to normal solutions. In the same table are given the approximate atomic volumes of the cations of the salt.

	At. vol.	$\eta$
Magnesium chloride . . . . .	14	1.2015
Cupric chloride . . . . .	8	1.2050
Manganous chloride . . . . .	7	1.2089
Nickel chloride . . . . .	7	1.2055
Cobalt chloride . . . . .	7	1.2041

It is obvious that for the atomic volumes of the same order of magnitude, the values of  $\eta$  are of the same order of magnitude; and, in general, the larger

<sup>1</sup> Ztschr. phys. Chem., 5, 35 (1890).

<sup>2</sup>  $\eta$ , the time of flow of water through the viscometer, is taken as unity.

the atomic volume the smaller the value of  $\eta$ , just as we should anticipate in terms of our hypothesis.

The small values of  $\eta$  for cadmium and mercury are due to the fact that the salts of these metals are only slightly dissociated.

Thallium seems at first glance to present an exception, but it is to be remembered that it is the thallos salt which produces the negative viscosity. The atomic volume curve deals with thallium in the thallic condition, and, consequently, thallium can not at present be considered as a test of our hypothesis.

#### CONCLUSIONS.

(1) We have measured the conductivities of various concentrations of copper chloride in water, methyl alcohol, ethyl alcohol, and in binary mixtures of these solvents. We have also measured the conductivities of various concentrations of potassium sulphocyanate in water, methyl alcohol, ethyl alcohol, acetone, and in binary mixtures of these solvents.

(2) Further, we have measured the fluidities of the above-named solvents and mixtures of these with one another; also the fluidities of solutions of potassium sulphocyanate in these solvents.

(3) A minimum in conductivity was observed in certain of the mixtures of the solvents. The hypothesis of Jones and Lindsay as substantiated by the work of Jones and Murray has been discussed.

(4) It has been shown that in nearly all cases where actual minima do not occur, there is nevertheless a decided dropping of the conductivity curves below the values as calculated from the rule of averages; and that this drop is most pronounced in the 25 per cent and 50 per cent mixtures, which are the points at which the actual minima usually occur. It has also been shown that these cases of dropping of the values below the values calculated from the rule of averages constitute cases of virtual minima, and we have extended the hypothesis of Jones and Lindsay to such cases, and have shown that the hypothesis when applied to the problem of conductivity in mixed solvents is perfectly general.

(5) A minimum in the fluidity curves of the above solvents has been observed, and the cause of this minimum has been explained as follows: It has been shown that viscosity and fluidity are largely frictional phenomena; and that since when two associated liquids are mixed they mutually decrease the association of one another, they thus increase the number of molecules present, and, consequently, increase the total frictional surface, thus causing an increase in viscosity (or decrease in fluidity). Further, it has been shown that the point of maximum viscosity is the point where the effect of the solvents upon each other is greatest; and, consequently, is the point at which we have the greatest number of simple molecules present. This has been

shown to be an additional proof of the hypothesis of Jones and Lindsay to account for the minima in conductivity.

(6) A maximum in conductivity has been observed similar to, and in the same solvents as the maxima in conductivity found by Jones and Bingham. The explanation offered by them to account for these maxima has been discussed, and it has been shown that their explanation only partly accounts for the facts. We have offered an additional explanation which is as follows: We have seen that at these maximum points of conductivity, the fluidity of the mixed solvent is also a maximum. We have shown that this maximum fluidity is due primarily to an increase in the size of the molecules of the solvents. We have shown further that this enlarging of the molecular spheres can not be due to increased association of either of the pure solvents, and must be due to a molecular aggregation of the solvents with one another. The conditions for such a molecular aggregation are probably most favorable in the particular mixtures in which the maximum fluidities occur. Since the fluidity of the solvent is increased, the velocity of the ions is increased; and, consequently, we conclude that the maxima in conductivity are dependent upon two factors—the change in the size of the ionic spheres, and the change in the fluidity of the solvent.

(7) We have shown that the dissociating action of any given solvent towards electrolytes is not dependent solely upon the physical properties of the solvent, but is also dependent upon the nature of the dissolved salt. That this is true is seen from the fact that although ternary electrolytes, in general, have a higher molecular conductivity when dissolved in water than binary electrolytes, yet when dissolved in methyl alcohol, or ethyl alcohol, or acetone, the conditions are exactly reversed; and the binary electrolytes show the greater molecular conductivities in these solvents. This is probably due to the breaking down of ternary electrolytes into their simplest ions in some solvents, while in other solvents they yield only two ions; whereas the binary electrolytes are dissociated in the same manner in all solvents.

(8) We have observed that the temperature coefficients of conductivity in the 25 per cent mixtures of the organic solvents with water are a maximum. This is probably due to the formation of more complex solvates between the dissolved substance and solvents in these particular mixtures than in any other mixtures of these solvents. These are the mixtures in which we have the simplest solvent molecules present, and, consequently, the most favorable conditions for the formation of solvates.

(9) We have observed a much greater molecular conductivity of potassium sulphocyanate in solutions in acetone than in aqueous solutions. We have shown that this might be due to either of two causes: (1) A greater degree of dissociation in acetone than in water. This view is untenable on account of the small association and dielectric constant of acetone as compared with that

of water. (2) A much greater velocity of the ions in acetone than in water. This has been demonstrated to be correct, since the fluidity of acetone is much greater than that of water, and especially because the solvates formed in water are much more complex than those in acetone, as is shown by the great difference in the temperature coefficients of conductivity. These are about ten times as great in aqueous solutions as they are in acetone solutions.

(10) A *negative coefficient of viscosity* has been found for potassium sulphocyanate in aqueous solution, and we have offered the following explanation to account for it, after having called attention to the fact that all previously offered explanations are inadequate.

From the experimental data recorded by Wagner we find that cæsium, rubidium, and potassium are practically the only ions that produce the negative viscosity in aqueous solution. We have further pointed out that all potassium salts do not give a negative viscosity, and that this is due to the fact that viscosity is an additive function of both the ions involved; and that in some cases the action of the anion, tending to produce a positive viscosity, is sufficient to overcome the action of the potassium ion which tends to produce a negative viscosity in aqueous solution. We have pointed out the fact that the total frictional surface in a liquid would be diminished by the introduction into that liquid of a substance which gives ions with atomic volumes much larger than the molecular volumes of the molecules of the liquid itself; and we find that such is probably the case when cæsium, rubidium, and potassium salts are dissolved in water.

We have tested our suggestion by reference to the atomic volume curve of the elements as drawn by Lothar Meyer, which, as is well known, shows that potassium, rubidium, and cæsium have by far the largest atomic volumes of any of the elements. We have still further tested our hypothesis by showing that the amount of negative viscosity produced by the chlorides of these three elements is in the same order as their relative atomic volumes.

## GENERAL SUMMARY AND CONCLUSIONS.

WE have now recorded the details in connection with seven investigations dealing with the condition of electrolytes in certain non-aqueous solvents, and in mixtures of these solvents with one another. At the conclusion of each investigation a brief summary of the facts and relations established by that investigation has been made.

It now seems desirable at the close of this monograph to give a general summary of the work done in this field, and the conclusions which can be drawn from it.

The *work of Lindsay* included the following solvents: Water, methyl alcohol, ethyl alcohol, and propyl alcohol, and mixtures of these with one another. The electrolytes which he dissolved in these solvents are potassium iodide, ammonium bromide, strontium iodide, cadmium iodide, lithium nitrate, and ferric chloride.

A *minimum* in the molecular conductivity was found for all the salts studied in mixtures of methyl alcohol and water, with the exception of cadmium iodide. A minimum was also found in the mixtures of ethyl alcohol and water especially at 0°, the minimum disappearing at 25°. Mixtures of methyl alcohol with ethyl alcohol do not show the minimum in conductivity, but in the 50 per cent mixture of these solvents the molecular conductivity of dissolved electrolytes is less than the mean of the conductivities in the separate solvents. An explanation that was offered to account for the conductivity minimum in the mixed solvents, is that in these associated solvents each solvent diminishes the association of the other. Since dissociating power is a function of the association of the solvent, anything that will diminish the association will diminish its dissociating power. The effect of mixing two dissociating solvents would thus be to diminish the association of both, and, consequently, the dissociating power of each of the solvents. A mixture of two such solvents would, then, dissociate less than either alone, and the conductivity of an electrolyte in such a mixture would be less than in the individual solvents — the conductivity curve would pass through a minimum.

This explanation would account for the conductivity minimum in the mixed solvents. The fundamental question, however, is this: Is this explanation correct?

We have now considered experimental evidence bearing upon this question. The molecular weights of the alcohol when dissolved in water are, in general, normal, *i. e.*, the molecules of the alcohol are the simplest possible. In pure

alcohols, however, the molecules are quite complex, as is shown by the surface-tension method of Ramsay and Shields. The water has thus broken down the complex molecules of alcohol into the simpler molecules.

A more direct line of evidence bearing upon this problem has been furnished by the work of Jones and Murray. They worked with mixtures of water, formic acid, and acetic acid each with the other. It will be recognized that these are all associated liquids. The molecular weight of each of these liquids dissolved in each of the other two was determined by the freezing-point method. It was found that the molecular weight was smaller the more dilute the solution, and even in the most concentrated solutions that could be studied, the molecular weight was always much less than the molecular weight of the substance when in the pure homogeneous condition. This showed beyond question that the action of an associated liquid is to diminish the association of another associated liquid.

The above explanation to account for the conductivity minimum in the mixed solvents is, then, undoubtedly an important factor. We shall, however, see that this is only one factor in conditioning the existence of this minimum.

The *investigation by Carroll* included the same solvents that had been used by Lindsay, *i. e.*, water, methyl alcohol, ethyl alcohol, and binary mixtures of these solvents; and in addition acetic acid was also used. The electrolytes employed by Carroll are cadmium iodide, sodium iodide, calcium nitrate, hydrochloric acid, and sodium acetate, in mixtures of acetic acid and water.

The minimum in the molecular conductivity was found for cadmium iodide, sodium iodide, and hydrochloric acid, in mixtures of methyl alcohol and water. The dissociation of sodium iodide, potassium iodide, and potassium bromide in a 50 per cent mixture of methyl alcohol and water was determined directly, and was found to be apparently slightly greater than in water alone at the same dilution.

The question as to the *cause of the minimum in conductivity* was then taken up. It was shown that there was a parallelism between the conductivity minimum and the minimum in the fluidity of the solvent. It was further shown that both minima are more pronounced at lower temperatures, and that both occur at approximately the same points. Again, the effect of rise in temperature is the same upon both minima, *i. e.*, a shift towards the mixture containing a greater per cent of alcohol.

From a quantitative study of these two classes of phenomena, the conclusion was drawn that the decrease in conductivity in electrolytes when dissolved in binary mixtures of various alcohols and water, which is frequently accompanied by a well-defined minimum in conductivity, is due largely to the diminution in the fluidity of the solvent which takes place when the two solvents are mixed. This diminishes the velocity with which the ions move, and, consequently, diminishes the conductivity.

A quantitative comparison is then made of the conductivity of the different solvents with their viscosities. In order that this comparison can be made for different solvents, we must deal with "comparable equivalent solutions," *i. e.*, solutions containing the same number of gram-molecules of electrolyte in the same number of gram-molecules of the different solvents.

The result is to show that conductivities of "comparable equivalent solutions" of binary electrolytes in such solvents as members of the methyl alcohol series, acetone, etc., are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factor of the solvent, or to the amount of the dissociation of the substance dissolved in that solvent.

This is essentially the same as to say that the hypothesis of Dutoit and Aston holds quantitatively for certain electrolytes in such solvents as water, methyl alcohol, and ethyl alcohol.

While the larger part of the *work of Bassett* had to do with the question of the relative velocities of the ions of silver nitrate in non-aqueous solvents, and in mixtures of these solvents with water and with one another, yet he took up the problem of the conductivity of silver nitrate in water, in methyl alcohol, in ethyl alcohol, and in binary mixtures of these solvents with one another.

It was shown that silver nitrate in mixtures of methyl alcohol and water gives a minimum in conductivity at both 0° and 25°. Silver nitrate, however, in mixtures of ethyl alcohol and water does not show the minimum at either 0° or 25°.

When the conductivities at 0° are compared with those of 25°, we see that the influence of one solvent on the other is greater the lower the temperature. This is exactly what would be expected in terms of the suggestion put forward in the work of Lindsay. As the temperature is raised the association of associated solvents becomes less and less; consequently, each solvent will diminish the association of the other less and less as the temperature becomes higher and higher.

The *investigation carried out by Bingham* included the solvents used in the earlier work — water, methyl and ethyl alcohols, and in addition acetone was employed. The conductivities of lithium nitrate, potassium iodide, and calcium nitrate in these solvents, and in binary mixtures of one with another, were measured. In this investigation a fairly large number of viscosity measurements were also made. These included not simply the measurement of the viscosities of the pure solvents and of the mixtures of these with one another, but also the viscosities of solutions of calcium nitrate in the different solvents and in the mixtures of these with one another. The temperature coefficients of conductivity and of fluidity in mixtures of acetone with the other solvents were also compared.

The conductivities in mixtures of acetone with water show the minimum previously observed in a number of cases. This minimum is closely connected with the minimum in fluidity observed in these mixtures.

The conductivities of potassium iodide in mixtures of methyl or ethyl alcohol with acetone, obey the rule of averages, and the conductivity curves are nearly straight lines at all the dilutions. In mixtures of acetone with the alcohols the fluidity curve is nearly a straight line.

One of the most important facts brought out in this investigation, and one that had not been observed in any of our previous work, is that lithium nitrate and calcium nitrate give a *very pronounced maximum* in conductivity in mixtures of acetone with methyl alcohol or ethyl alcohol. It was pointed out that this must be due either to an increase in the dissociation, increasing the number of ions present, or to a diminution in the size of the ionic spheres, causing the ions present to move more rapidly. It was shown to be possible to eliminate one of these.

The fluidities of mixtures of acetone with the alcohols were shown to obey the rule of averages, which would indicate that there is no increase in the molecular aggregation when the alcohols and acetone are mixed. In terms of the well-established hypothesis of Dutoit and Aston, such a mixture would not dissociate to a greater extent than the constituent solvents. Further, direct measurements of dissociation at extreme dilutions have failed to show any great difference between the dissociating power of the mixtures and that of the pure solvents. Further, the maximum moves from the 25 per cent mixture at large concentration to the 75 per cent mixture in the more dilute solutions. This would not be expected if the dissociating power is greatest in a certain mixture.

We have thus eliminated increase in dissociation as being the cause of the maximum and are compelled to accept the other alternative, that the maximum in conductivity is due to a change in the dimensions of the atmospheres about the ions.

In dealing with conductivity in single solvents and in mixtures of these with one another, we must take into account not only the effect of each constituent of the mixture on the association of all the other constituents, and the viscosity of the individual solvent or solvents, but also the sizes of the spheres of the solvents around the ions, and any changes in the sizes of these spheres in different mixtures of the solvents.

These ionic spheres, or solvates, have been shown by Jones to exist generally in solutions, and the ions must drag these spheres with them in their movements under the action of the current.

Any change in the size of these spheres would produce a change in the effective mass of the ion, and, consequently, a change in the velocity with which it would move.



It was also shown in this investigation that the hyperbola, and not the straight line, is the normal curve of viscosity.

While the *work of Rouiller* had to do more especially with the velocities of ions in mixed solvents, yet he studied the conductivities of silver nitrate in acetone, in mixtures of acetone with water, in mixtures of methyl alcohol with ethyl alcohol, in methyl alcohol and acetone, and in ethyl alcohol and acetone.

Silver nitrate, in mixtures of methyl alcohol and acetone, and ethyl alcohol and acetone, shows a pronounced maximum in conductivity strictly analogous to calcium nitrate, which had been studied in these solvents by Bingham. This maximum is pronounced at both 0° and 25°, appearing in the 25 per cent acetone mixture in the more concentrated solutions, and shifting with increase in dilution through the 50 per cent to the 75 per cent mixture.

The work of Rouiller on the migration velocity of ions in mixtures of these solvents would indicate that the explanation of the conductivity maximum offered by Jones and Bingham is correct—there is a change in the atmosphere of the solvent about the ions.

The *investigation of McMaster* included the same solvents that had been used by Bingham—water, methyl alcohol, ethyl alcohol, and acetone, and binary mixtures of these solvents.

The electrolytes used were lithium bromide and cobalt chloride. The conductivities of a large number of solutions of these substances in the above solvents and in binary mixtures of these solvents were measured.

The fluidities of water, methyl alcohol, ethyl alcohol, and acetone, and binary mixtures of these solvents, were also measured. The conductivities in mixtures of the alcohols with water, and in the mixtures of acetone with water, show a well-marked minimum. This minimum in conductivity was more pronounced at the lower temperature, and was intimately connected with the minimum in fluidity observed in the above mixtures.

The conductivity curves in mixtures of methyl and ethyl alcohols are nearly straight lines, obeying the law of averages, as we should expect. Lithium bromide dissolved in mixtures of methyl or ethyl alcohol with acetone, shows a pronounced maximum in conductivity. The conductivity maximum was also given by cobalt chloride in mixtures of acetone with ethyl alcohol.

The fluidities of lithium bromide in mixtures of acetone with the alcohols were found to be what would be expected from the rule of averages—the fluidity curves being nearly straight lines. The same was found for the pure solvents. This would indicate that the alcohols and acetone do not form more complex aggregates when mixed than when alone.

We are therefore forced to the same conclusion as that reached by Jones and Bingham, *i. e.*, that the size of the ionic spheres is an important factor in determining conductivity, and that changes in the sizes of these spheres in

different mixtures of the solvents are the prime factor in conditioning the maximum in the conductivity curve.

Some interesting results were obtained in this investigation bearing on the *temperature coefficients of conductivity*.

Jones<sup>1</sup> has recently pointed out the bearing of hydrates on the temperature coefficients of conductivity. Jones and West showed that with rise in temperature there is a decrease in the dissociation, and that increase in conductivity with rise in temperature was due primarily to an increase in the velocities with which the ions move. As the temperature is raised the hydrates in combination with the ion become simpler and simpler, and, therefore, the effective mass of the ion decreases with rise in temperature. The ion being smaller and the solvent less viscous, it will move faster the higher the temperature.

Jones has also pointed out in terms of his hydrate theory that the greater the dilution the greater should be the temperature coefficient of conductivity. The more dilute the solution, the more complex the hydrate; the more complex the hydrate in combination with any given ion, the greater the change in the complexity of the hydrate with rise in temperature. The temperature coefficient of conductivity should, therefore, be greater in the more dilute solution, and such is the fact. The work of McMaster showed that the temperature coefficients of conductivity and of fluidity for lithium bromide are of the same order of magnitude, the temperature coefficients for this substance in the mixed solvents all being positive.

In certain of the mixtures of acetone with the alcohols, cobalt chloride showed *negative temperature coefficients of conductivity*. This was true in the 75 per cent mixture of acetone with methyl alcohol, and also in the 50 per cent and 75 per cent mixtures of acetone with ethyl alcohol. Negative temperature coefficients had previously been found in a few cases at low temperatures, but in this work negative temperature coefficients were found at ordinary temperatures.

What is the meaning of negative temperature coefficients of conductivity? With rise in temperature the solvent becomes less viscous, and this would increase the velocity of the ions. With rise in temperature, however, the association of the solvent becomes less and, consequently, its dissociating power is diminished; which means that there would be a smaller number of ions present the higher the temperature. These two influences act counter to one another — the former increasing the conductivity and the latter diminishing it.

When we have negative temperature coefficients of conductivity, it means that the latter influence more than overcomes the former — the decrease in the number of the ions with rise in temperature more than counterbalancing

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<sup>1</sup> Carnegie Institution of Washington, Publication No. 60.

the effect on conductivity of the increased velocity with which the ions move. The result is a decrease in conductivity with rise in temperature.

This explanation accounts entirely satisfactorily for the facts in the above case. The alcohols and acetone are at ordinary temperatures highly associated liquids. The effect of rise in temperature is to diminish their association and, consequently, their dissociating power.

It is interesting to note in this connection that a solution was found that had a *zero temperature coefficient of conductivity*. It was a solution of cobalt chloride in a 75 per cent mixture of acetone with methyl alcohol, the solution having a value of  $v = 200$ .

The last investigation upon this problem—*that of Veazey*—has brought out a number of points of interest. It consisted experimentally in measuring the conductivities and viscosities of solutions of copper chloride and potassium sulphocyanate in water, methyl alcohol, ethyl alcohol, and acetone, and in binary mixtures of these solvents.

The minimum in conductivity observed in the earlier investigations was found for the above substances, and was shown to be a much more general phenomenon than was supposed from any of the earlier work. It has been pointed out that the minima in fluidity, or maxima in viscosity, correspond to the minima in conductivity of the solutions of electrolytes in these solvents. An explanation of why solutions of methyl alcohol or ethyl alcohol and water are more viscous than either of the pure solvents alone was offered.

These liquids are all highly associated. When one associated liquid is mixed with another associated liquid, each diminishes the association of the other. This means that the large molecules of each solvent are torn down into a larger number of small molecules. This would increase the frictional surfaces of the molecules that would be exposed to one another, just as small shot would exert greater friction, in moving over one another in a manner analogous to that followed by the molecules in producing viscosity, than larger shot. The result of each associated liquid diminishing the association of the other, would thus be to increase the viscosity of the mixture over that of either pure solvent.

This explains also why the conductivity curves for different dilutions of the same substance generally approach one another as they approach the minimum. Those mixtures of the solvents in which the conductivity minima occur are the least associated, and, therefore, have the least dissociating power. It is obvious that such mixtures would produce the least increase in dissociation with increase in dilution, and, consequently, the conductivity curves for the different dilutions would approach one another as they approach the minima. Fact and theory are here in perfect accord.

The minima in conductivity observed in the earlier work were also found in a number of cases studied in this investigation. It was shown that this is

due in part to a change in the size of the ionic spheres, but that another factor also comes into play.

It was found that the maxima in conductivity correspond to the maxima in fluidity of the mixed solvents. These maxima in fluidity are probably due, as has been shown, to an increase in the size of the molecules of the solvent. From the work of Jones and Murray this can not be caused by an increased association of the molecules of the several solvents, since the action of each solvent on the other is to diminish its association. This increase in size of the molecular aggregates of the solvents must be due to the combination of one solvent with the other, forming a molecular complex. This would diminish the viscosity, or increase the fluidity, and, consequently, increase the velocity with which the ions would move through the solvent. This factor must also be taken into account in explaining the conductivity maxima observed in a number of these investigations.

A reason is suggested to account for the fact that different solvents show different relative dissociating powers in the case of binary and ternary electrolytes. Weakly dissociating solvents are probably capable of breaking down ternary electrolytes into only two ions; while strongly dissociating solvents can break these molecules down into three ions. This would also explain why ternary electrolytes, showing greater conductivity in water than binary electrolytes, often show much smaller conductivity in the alcohols and in acetone than binary electrolytes.

The temperature coefficients of conductivity are a maximum in the 25 and 50 per cent mixtures of the organic solvents with water. These are about the mixtures in which the solvents show least association — the molecules would be in the simplest condition and therefore most favorable for chemical action. The solvents probably combine with the dissolved substance to the greatest extent in such mixtures, and the effect of rise in temperature, breaking down these complexes, would therefore be a maximum.

The conductivity of solutions of potassium sulphocyanate in substances like acetone is much greater than in water. This was proved to be due to the greater fluidity of the acetone. Potassium sulphocyanate dissolved in water lowers the viscosity of water, *i. e.*, the solution has a smaller viscosity than water itself. On examining the literature it was found that salts of potassium, rubidium, and cæsium are practically the only known electrolytes which lower the viscosity of water when dissolved in it. Certain salts of potassium, however, do not lower the viscosity of water, just as might be expected, since viscosity is an additive property of both the ions present in the solution. The anions tend to increase the viscosity of the solution, while certain cations, *viz.* potassium, rubidium, and cæsium, have a tendency to diminish the viscosity of a solution. If the effect of the negative ion more than overcomes that of the positive ion, potassium, rubidium, and cæsium, then the solution is

more viscous than water. If it does not, then the solution is less viscous than pure water.

The explanation of the diminution in viscosity produced by the above-named cations is comparatively simple in the light of the conception of viscosity proposed earlier in this investigation. If the atomic volume of the ions introduced was much larger than the molecular volumes of the solvent molecules, the effect would be to diminish the frictional surfaces that would come in contact with one another in the solution, and, consequently, the friction of the movement of the molecules over one another would be diminished. The question, then, is: Are the atomic volumes of potassium, rubidium, and caesium very large? And are they much larger than the atomic volumes of other elementary cations?

If we turn to the well-known atomic volume curve, we see that potassium, rubidium, and caesium occupy the maximum of the curve, and have much larger atomic volumes than any other known elements. Even the atomic volume of potassium, which is smaller than that of rubidium and caesium, is much larger than that of any other known element except rubidium and caesium.

If we test this relation quantitatively, the result is very satisfactory. By comparing the viscosities of solutions of the same concentration of potassium chloride, rubidium chloride, and caesium chloride, we find that, while all these viscosities are less than the viscosity of pure water, the viscosity of the solution of rubidium chloride is less than that of potassium chloride, and the viscosity of the solution of caesium chloride is less than that of rubidium chloride.

More work will be done in the physical chemical laboratory of the Johns Hopkins University to test whether these relations are perfectly general.

In conclusion it gives me great pleasure to express my hearty thanks to my seven coöperators, who, the one after another, have taken up and studied uninterruptedly during the past six years the various problems that have arisen in connection with this line of investigation.



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