1924

Conductivity and ionization of certain salts in absolute alcohol

Armin Brene Jewell

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CONDUCTIVITY AND IONIZATION OF CERTAIN SALTS IN ABSOLUTE ALCOHOL

A

THESIS

Submitted to the Faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
DEGREE OF
MASTER OF SCIENCE IN CHEMICAL ENGINEERING

by
Armin Brene Jewell

Rolla, Missouri
1924

Approved by
Thesis: Conductivity and ionization of certain salts in absolute alcohol.
Jewell. 1924.
The writer wishes to express his appreciation of the generous and ready assistance given by the members of the chemistry department. Their many suggestions as to technic and development have proved of inestimable value.

He also takes this opportunity to thank Mr. R.F. Grady and Mr. W.O. Keeling. He is indebted to Mr. Grady for the use of his amplification apparatus and to Mr. Keeling for the data on solubility. Mr. Keeling also devised the method for the preparation of the aluminum amalgam and collaborated with the writer in the purification of the alcohols and salts.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foreword</td>
<td>1</td>
</tr>
<tr>
<td>Historical Review</td>
<td>4</td>
</tr>
<tr>
<td>Apparatus</td>
<td>12</td>
</tr>
<tr>
<td>Materials</td>
<td>18</td>
</tr>
<tr>
<td>Experimental Data</td>
<td>21</td>
</tr>
<tr>
<td>Data</td>
<td>25</td>
</tr>
<tr>
<td>Graphs</td>
<td>31</td>
</tr>
<tr>
<td>Discussion</td>
<td>43</td>
</tr>
<tr>
<td>Summary</td>
<td>49</td>
</tr>
<tr>
<td>Bibliography</td>
<td>50</td>
</tr>
<tr>
<td>Index</td>
<td>56</td>
</tr>
</tbody>
</table>
ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Illustration</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wiring Diagram for Amplifier</td>
<td>13</td>
</tr>
<tr>
<td>Wiring Diagram for Bridge</td>
<td>16</td>
</tr>
<tr>
<td>Laboratory</td>
<td>17</td>
</tr>
</tbody>
</table>
HISTORICAL REVIEW

The idea of investigating the conductivity of non-aqueous solutions is by no means a new one, for as early as 1883, Stephan (1) made a number of conductivity measurements using as a solvent mixtures of alcohol and water. In this same year, Grossman (2), following Stephan's procedure, did some work on conductivity and viscosity of alcoholic mixtures and formulated a relation between these quantities. In 1887, Arrhenius (3) extended somewhat the work of Stephan and Grossman when he worked with aqueous solutions to which had been added small quantities of such non-electrolytes as acetone and methyl alcohol.

Viscentini, in 1885, (4) determined the conductivity of a number of salts in ethyl alcohol.

This investigation may be termed the first work upon a strictly non-aqueous solvent although in a sense the solvent was not non-aqueous in that Viscentini did not follow an elaborate procedure to secure an anhydrous alcohol. Hartwig (1), also studied the conductivity of salts in ethyl alcohol as well as a number of organic acids in both methyl and ethyl alcohols.

In the next few years the number of investigators as well as the scope of their work was considerably increased. Cattaneo (2), worked with salts in ethyl alcohol and found that a number of those with which he worked had negative temperature coefficients. Paschoow (3), in 1892, worked with potassium iodide, cadmium iodide, calcium iodide, potassium acetate, and sodium acetate using methyl alcohol as a solvent and in the year following, Holland (4), investigated the effect of certain non-electrolytes upon the conductivity of various salts in methyl alcohol.

(3) Charcow.
Fitzpatrick (1), in the year following Holland's work, studied the conductivity of calcium and lithium nitrates and chlorides in methyl and ethyl alcohols and found values which were considerable although less than the values of the conductivities of the same salts in aqueous solutions. Vollmer (2), in 1894, studied several salts over a wide range of dilution and Carrara (3) two years later carried out an extensive investigation of the conductivities of a large number of salts in methyl alcohol.

Before going further in the review of the work done on the lower aliphatic alcohols it may be well to mention the work of Schlamp (4) who in 1894 made a few measurements on the higher alcohols, as well as that of Carrara (5) and Kablukoff (6) who carried out a somewhat more extensive investigation of these alcohols.

(1) Phil. Mag. 24: 378.
Continuing with the work done on the lower alcohols, the researches of Dutoit and Aston (1) as well as those of Dutoit and Friderich (2) deserve mention. Dutoit and Aston came to the conclusion that the dissociating power of a solvent is a direct function of its degree of association in the pure state. This relation was found to hold in a number of cases but later investigators have pointed out a number of important exceptions to it. Euler (3) showed that potassium iodide and certain other salts gave considerable values of conductivity in non-associated solvents such as nitrobenzene while in certain organic acids which are highly associated such as butyric acid the conductivity is small. Jones pointed out that the facts as found by Euler "supported the hypothesis proposed by Thompson and Nernst (4) which attributes the dissociating power to the high dielectric constant of the medium;" but Eversheim (5) and Tilden and Gentnerzwer (6) have shown that, although liquid

(5) Ann. der Phys. 8: 539.
sulphur dioxide has a small dielectric constant it gives a high conductivity. Some time later Plotnikow (1) showed that the dissociation is somewhat dependent on the character of the dissolved substance.

A large and interesting work on about thirty organic solvents has been done by Walden. A great number of papers have come from his laboratory dealing with the relation between conductivity, viscosity, solvent power etc. The titles and references to these papers will be found in the bibliography.

In 1896, Zelinsky and Krapiwin (2) first noted a minimum in conductivity on mixing methyl alcohol and water. A little later Cohen (3) noted a minimum in conductivity when a dilute solution of potassium iodide was dissolved in ethyl alcohol and water. Following the work of these investigators, Jones and collaborators made a series of conductivity determinations on non-aqueous solutions extending over a period of years. The results of these investigations will be considered in more or less detail.

In 1902, Jones and Lindsay (1) studied the conductivity of certain salts in water, methyl, ethyl, and propyl alcohols and mixtures of these solvents. The values that they obtained during the course of this investigation compared favorably with those previously obtained by Zelinsky and Krapiwin. Jones and Carroll (2), continuing on similar lines, extended the work of Jones and Lindsay and attempted to establish some relation between conductivity and viscosity. They formulated the hypothesis that decrease in conductivity is caused either by decrease in dissociation or decrease in ionic mobility. They further showed that decrease in dissociation was out of the question and came to the conclusion that the lessened conductivity was due to a decrease in ionic mobility. Jones and Carroll also showed that the less the viscosity the greater is the conductivity.

Jones and Bingham (3) in the following year established the fact that in general conductivity curves were nearly straight lines.

(3) Am. Chem. J. 34: 481.
Two papers appeared from the John Hopkins laboratory in 1906, one by Jones and Mc Master (1) showing the variation of temperature coefficients with the dilution and the other by Jones and Rouiller (2) upon the conductivities and relative migration velocities of silver nitrate ions in several alcohols. In 1907, Jones and Veazy (3) measured the conductivity and viscosity of copper chloride and potassium sulphocyanate in water, methyl alcohol, ethyl alcohol, and acetone.

One of the most valuable contributions to the literature of conductivity appeared from the pen of Turner (4) in 1908. Turner found the value of the limiting conductivity and the degree of ionization of a number of alcoholic solutions. He also pointed out several errors into which previous investigators had fallen and suggested how these might be remedied. Turner’s paper will again be referred to later.

No article of interest appeared after Turner's paper until 1911 when Jones and Kreider (1) studied the dissociation of electrolytes and non-aqueous solvents by both conductivity and boiling point methods. They compared the ratios of the limiting conductivities of certain salts in two different solvents with the ratios of the fluidities of these solvents. This article completed the work of Jones who perhaps more than any other one investigator has contributed most to the literature of conductivity in non-aqueous solution. The complete results of Jones' work may be found in Carnegie Institute Publication No. 80.

More recently Robertson and Acree (2) in 1915 have made conductivity measurements on ethyl alcohol solutions, and still later Danner and Hildebrand (3) have done considerable work on the degree of ionization of alcohol. This paper by Hildebrand is the last important article appearing on ionization in alcoholic solution as determined by conductivity methods, although recent investigators have done some little work on the ionization of alcohols by potential and esterification methods.

APPARATUS

BRIDGE:— The bridge used was of the extended coil type. One half meter of the wire in the center of the bridge was graduated in millimeters while the other nine and one half meters were contained in non-inductive coils at either end. Transfer from the short bridge to the long was readily accomplished by means of plugs.

RESISTANCE:— A standard Manganin resistance was used for the most part. In some cases, however, it was necessary to use additional resistances but these were checked against the first resistance in all cases. The resistance of the lead wires was also determined but was small compared to the total resistance used thus making a correction unnecessary.

MICROPHONE HUMMER:— A microphone hummer was used as a source of high frequency current. The current delivered was not a pure sine wave but a wave of this type was approximated and a good minimum was obtained in most cases. The frequency used was 1000.

AMPLIFIER:— An ordinary homemade two-stage radio amplifier was used to make the signals more audible.
WIRING DIAGRAM FOR AMPLIFIER
HEADPHONES:— A pair of 2000 ohm Baldwin headphones were used in connection with the amplifier.

THERMOSTAT:— The thermostat employed was of the de Khotinsky type and temperature control within a few thousandths of a degree was possible.

MIXING APPARATUS:— The mixing apparatus consisted of several round boards mounted upon a common shaft. These boards were fitted with clamps to which tubes containing the alcohols and salts could be fastened and the whole rotated by means of a small motor. The effect of this contrivance was to secure rapid and thorough mixing by rotating the tubes in an end-over-end fashion. Efficient temperature control was also attained as the tubes were completely immersed in the bath.

CONDUCTIVITY CELL:— A Washburn type No. 2 cell for dilute solutions was used. The electrodes were platinized.
THE CIRCUIT:— An attempt was made to reproduce as nearly as possible an ideal circuit as outlined by Washburn (1). The requirements which Washburn gives for such a circuit are:

1. Use of a pure sine wave.
2. Use of a telephone tuned to the circuit used.
3. Use of resistance units free from inductance and capacity.
4. Electromagnetic shielding.

The wiring diagram for the circuit used is given on the following page. It will be noted that a capacity has been inserted in both arms of the bridge. The purpose of this was to equalize the capacity effect in the two arms and a marked improvement in the point of minimum was noted as soon as the addition of these capacities was made.

Polarization, which manifests itself in the appearance of a poor minimum, may be compensated for either by the use of a higher frequency or by platinizing the electrodes. The frequency of the hummer could not be changed but the electrodes were platinized. Whether the decrease in polarization obtained in this way offset the resulting increase in absorption is questionable. The question of absorption will again be referred to later.

WIRING DIAGRAM

KOHLRAUSCH BRIDGE
Electromagnetic shielding was accomplished by grounding the circuit in several places and by placing a grounded screen under the bridge. This shielding produced an improvement in the minimum but screening the amplifier as well had no further effect. Winding the telephone cord with small copper wire which was grounded, however, was found necessary.

The lead wires from the conductivity cell were not connected directly to the bridge but instead a pair of mercury-filled tubes dipping into the bath were used as an intermediary. Wires with amalgamated ends led from the cell to the tubes and then from the tubes to the bridge. The purpose of this arrangement was to prevent heat exchange between the electrodes and the lead wires.
MATERIALS

PREPARATION OF ALUMINUM AMALGAM:— The amalgam was prepared by heating fairly large pieces of aluminum with mercury in a flask fitted with a reflux condensor for several hours. It was then removed from the flask and stored in stoppered bottles. An excellent yield of amalgam was obtained in this way. Better yields were obtained by using rather large pieces of aluminum than with chips or shavings. This was probably due to the fact that the larger pieces sank down farther into the mercury thus coming into more intimate contact with it.

Heating the mercury and aluminum in an atmosphere of carbon dioxide was also tried but the results obtained did not justify the trouble.

LIME:— The lime used was heated from eight to ten hours at a temperature of 600° to 700° C. and placed in flasks while still hot.

PURIFICATION OF SALTS:— In general the ordinary C.P. salts were used without treatment other than being thoroughly dried and then stored over phosphorous pentoxide.
The potassium chloride which was used in determining the cell constant, however, was obtained by precipitating C.P. KCL with HCL and then crystallizing this product twice. This salt was free from sodium and other impurities.

DEHYDRATION OF ALCOHOLS:— All of the alcohols were treated in essentially the same manner except that it was necessary to substitute an oil bath for the water bath in the case of propyl alcohol.

Three-liter flasks containing a quantity of the previously heated lime were filled with the alcohol to be treated and allowed to stand for several days. The flasks were then fitted with condensers and after the addition of a small quantity of sodium hydroxide to remove aldehydes, were refluxed on the water bath for about eight hours. This product was then distilled and allowed to stand over aluminum amalgam with frequent shaking for several days. This last treatment removed the last traces of water.

After the evolution of gas had stopped, the alcohol was placed in a thoroughly dried flask fitted with a dry condenser and receiver and distilled. The first and last portions of the distillate were rejected.

Special precautions were taken to distill the alcohol in a dry atmosphere. The receiver was a 500 c.c. separatory funnel fitted directly on to an adapter.
All of the connections were made air-tight with the exception of one opening which was guarded by a tube of calcium chloride.

Previous to the time of distillation, one inch test tubes were drawn out to a funnel opening and thoroughly cleaned and dried. A small quantity of salt was then placed in these tubes and then they were filled with alcohol from the receiver and immediately sealed. Alcohol for dilution purposes was also tubed in the same way. The total time which the alcohol was in contact with the outside air was probably not more than ten seconds.

Alcohol prepared in this manner showed a constant boiling point and had a specific conductivity comparing favorably with that obtained by other investigators.

CONDUCTIVITY WATER:— The ordinary distilled water of the laboratory was used as conductivity water except that the precaution was taken of collecting this water directly from the still and then boiling it to remove dissolved gases. It was stored in seasoned pyrex flasks. The water treated in this manner had an average specific conductivity of $2 \times 10^{-5}$. 
CELL CONSTANT:— The cell constant was determined after the method of Kraus and Parker (1) who found that a 0.1 N solution of KCl gave much more accurate results than the 1/50 N solution usually employed for this purpose.

A one-liter volumetric flask previously cleaned with cleaning solution and live steam and then rinsed repeatedly with distilled water was filled to the mark in the thermostat maintained at 20°C. with conductivity water and the weight of the water calculated from the density of water at that temperature. The weight of the water was then multiplied by the factor 0.0074945, the value determined by Kraus and Parker, which gave the weight of KCl required. This amount of the specially prepared KCl was quickly weighed out to the exact quantity calculated, added to the water and the flask kept stoppered.

The mean value obtained by Kraus and Parker for the specific conductance of 0.1 N KCl solution at 25°C. is 0.0128988. Using this value, the cell constant was found to be 0.058861. A check solution prepared from the ordinary C.F. KCl gave a value $k = 0.05887$.

The cell constant was redetermined at frequent intervals and found to remain the same.

EXPERIMENTAL:—One question of importance in working with alcoholic solutions has to do with the possible oxidation of the alcohol to acetic acid during the experiment. This was found to be not serious. Turner (1) investigated this phenomenon and found that the gain in conductivity during the course of an experiment could not be greater and one or two hundredths of a reciprocal megohm.

The action of alcohol on glass is much smaller than water. The specific conductivity of a sample of alcohol kept in ordinary glass for twenty-six days increased only $1 \times 10^{-7}$.

A very marked effect, and one which caused several determinations to be remade, was observed upon placing alcohol in the conductivity cell which had been cleaned and dried in the ordinary way. Turner had previously noted this phenomenon and came to the conclusion that drying either "loosened the surface of the glass" or that the solvent action was so much increased at the higher temperature that even in the short time which the drops of water remained on the glass enough of it was acted upon to greatly increase the conductivity of the alcohol which was afterward put in the vessel. This source of error was avoided by rinsing the cell several times with alcohol and then allowing it to stand full of alcohol for twelve hours.

Flatinized electrodes in alcoholic solutions seem to show a certain amount of absorption and for this reason it would probably have been better to have used bright electrodes had they been available. This difficulty, however, was overcome to some extent by allowing the solution to stand in the cell for a time.

The following procedure was finally adopted after a number of trials to find the best method. The tubes of salt and alcohol were placed in the stirring apparatus and rotated for several hours and then removed and allowed to float in the bath until all of the undissolved salt had settled to the bottom of the tubes. This also allowed the upper ends of the tubes to dry. The tip of one of the tubes was then broken and a quantity of the alcohol drawn directly into the conductivity cell. Moisture and carbon dioxide from the breath were excluded from the cell by a tube containing a quantity of calcium chloride and soda lime. After the cell had been rinsed several times in this manner, it was refilled and the conductance determined.

In making the conductance measurements, three different resistances and bridge readings were taken and the mean of these used to calculate the specific conductivity.

The pure alcohol was then removed from the cell and a quantity of the saturated alcoholic solution treated in the same manner. After the conductance of this
solution had been determined, it was removed from the cell and placed in one of a number of long-necked glass-stoppered flasks almost completely submerged in the bath. The various dilutions were made in these flasks by means of a number of pipettes. The pipettes were kept dry and at a constant temperature while not in use by placing them in stoppered tubes immersed in the bath. The ends of the pipettes were also protected by calcium chloride-soda lime tubes.

All determinations were made in duplicate and excellent check results were obtained with the exception of the potassium sulphate solutions which will be discussed later. With values of the order of $10^{-5}$, checks in the fourth characteristic figure were not uncommon.
In the pages following, the average corrected specific conductivity is the mean of two independent determinations corrected for the conductance of the pure solvent.

"V" is the volume of solvent containing one mol of the solute and has been computed from the solubility value and the specific gravity of the alcohol at that temperature. The specific gravities were taken from Bureau of Standards Bulletins.

The limiting molecular conductivity has been determined by extrapolating a conductivity curve to zero concentration.

The usual assumption that \( \frac{\kappa}{\kappa_0} \) equals the fraction of salt ionized has been made.
### Methyl Alcohol–Potassium Chloride 25°

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp.K.</th>
<th>( \mu )</th>
<th>( \alpha )</th>
</tr>
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<tbody>
<tr>
<td>17.84</td>
<td>0.5311</td>
<td>0.003449</td>
<td>61.5</td>
<td>0.482</td>
</tr>
<tr>
<td>23.80</td>
<td>0.3983</td>
<td>0.002711</td>
<td>64.5</td>
<td>0.506</td>
</tr>
<tr>
<td>47.60</td>
<td>0.1992</td>
<td>0.001478</td>
<td>70.4</td>
<td>0.552</td>
</tr>
<tr>
<td>95.20</td>
<td>0.0996</td>
<td>0.007995</td>
<td>76.9</td>
<td>0.603</td>
</tr>
</tbody>
</table>

\( \nu_\infty = 127.5 \)

### Methyl Alcohol–Potassium Chloride 30°

<table>
<thead>
<tr>
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<th>( \alpha )</th>
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<tr>
<td>17.57</td>
<td>0.5407</td>
<td>0.003774</td>
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<td>0.002104</td>
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<td>0.499</td>
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<td>70.28</td>
<td>0.1352</td>
<td>0.001158</td>
<td>81.4</td>
<td>0.550</td>
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<tr>
<td>140.56</td>
<td>0.0676</td>
<td>0.000632</td>
<td>88.8</td>
<td>0.600</td>
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<td>281.12</td>
<td>0.0328</td>
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\( \nu_\infty = 148.0 \)

### Methyl Alcohol–Potassium Chloride 35°

<table>
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<th>( \mu )</th>
<th>( \alpha )</th>
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<tr>
<td>16.52</td>
<td>0.5762</td>
<td>0.004050</td>
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<td>0.442</td>
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<td>33.04</td>
<td>0.2881</td>
<td>0.002241</td>
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<td>0.489</td>
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<td>66.08</td>
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<td>0.001240</td>
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<td>0.541</td>
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<td>264.32</td>
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<td>528.64</td>
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<td>0.000197</td>
<td>104.2</td>
<td>0.688</td>
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\( \nu_\infty = 151.5 \)
### Methyl Alcohol–Potassium Nitrate 25°

<table>
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<th>$V$</th>
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<td>137.70</td>
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<td>275.40</td>
<td>0.0466</td>
<td>0.000332</td>
<td>91.4</td>
<td>.548</td>
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</table>

$\nu_\infty = 166.7$

### Methyl Alcohol–Potassium Nitrate 30°

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<th>$\alpha$</th>
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<td>0.001253</td>
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<td>.412</td>
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<td>248.0</td>
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<td>496.0</td>
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<td>992.0</td>
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<td>0.000115</td>
<td>113.6</td>
<td>.602</td>
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</table>

$\nu_\infty = 188.7$

### Methyl Alcohol–Potassium Nitrate 35°

<table>
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<th>$C$</th>
<th>Sp.K.</th>
<th>$\nu_V$</th>
<th>$\alpha$</th>
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<tbody>
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<td>28.50</td>
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<td>70.7</td>
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<tr>
<td>57.00</td>
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<td>114.0</td>
<td>0.1132</td>
<td>0.000790</td>
<td>90.1</td>
<td>.423</td>
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<td>228.0</td>
<td>0.0566</td>
<td>0.000439</td>
<td>100.2</td>
<td>.470</td>
</tr>
<tr>
<td>456.0</td>
<td>0.0283</td>
<td>0.000242</td>
<td>110.5</td>
<td>.519</td>
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<td>912.0</td>
<td>0.0141</td>
<td>0.000133</td>
<td>121.5</td>
<td>.570</td>
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$\nu_\infty = 213.0$
### Ethyl Alcohol–Potassium Chloride 25°

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<th>$\alpha$</th>
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<td>314.3</td>
<td>0.0302</td>
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<td>.467</td>
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<td>0.0075</td>
<td>0.0000309</td>
<td>38.8</td>
<td>.574</td>
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<td>2514.4</td>
<td>0.0038</td>
<td>0.0000174</td>
<td>42.1</td>
<td>.623</td>
</tr>
</tbody>
</table>

$\nu_\infty = 67.6$

### Ethyl Alcohol–Potassium Chloride 30°

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp. K.</th>
<th>$\nu_v$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>0.0317</td>
<td>0.0001081</td>
<td>32.5</td>
<td>.351</td>
</tr>
<tr>
<td>602</td>
<td>0.0158</td>
<td>0.0000615</td>
<td>37.0</td>
<td>.400</td>
</tr>
<tr>
<td>1204</td>
<td>0.0079</td>
<td>0.0000337</td>
<td>40.6</td>
<td>.439</td>
</tr>
<tr>
<td>2408</td>
<td>0.0040</td>
<td>0.0000188</td>
<td>45.2</td>
<td>.488</td>
</tr>
<tr>
<td>4816</td>
<td>0.0020</td>
<td>0.0000103</td>
<td>49.6</td>
<td>.536</td>
</tr>
<tr>
<td>9632</td>
<td>0.0010</td>
<td>0.0000057</td>
<td>55.3</td>
<td>.596</td>
</tr>
</tbody>
</table>

$\nu_\infty = 92.6$

### Ethyl Alcohol–Potassium Chloride 35°

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp. K.</th>
<th>$\nu_v$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>289.2</td>
<td>0.0332</td>
<td>0.0001233</td>
<td>35.7</td>
<td>.278</td>
</tr>
<tr>
<td>578.4</td>
<td>0.0166</td>
<td>0.0000708</td>
<td>40.9</td>
<td>.320</td>
</tr>
<tr>
<td>1156.8</td>
<td>0.0083</td>
<td>0.0000400</td>
<td>46.3</td>
<td>.361</td>
</tr>
<tr>
<td>2313.6</td>
<td>0.0041</td>
<td>0.0000225</td>
<td>52.0</td>
<td>.406</td>
</tr>
<tr>
<td>4627.2</td>
<td>0.0021</td>
<td>0.0000127</td>
<td>58.7</td>
<td>.458</td>
</tr>
<tr>
<td>9254.4</td>
<td>0.0010</td>
<td>0.0000071</td>
<td>65.8</td>
<td>.514</td>
</tr>
</tbody>
</table>

$\nu_\infty = 128.2$
<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp. K.</th>
<th>( \eta )</th>
<th>( \alpha )</th>
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</thead>
<tbody>
<tr>
<td>332.7</td>
<td>0.0387</td>
<td>0.0000892</td>
<td>29.7</td>
<td>0.448</td>
</tr>
<tr>
<td>565.5</td>
<td>0.0193</td>
<td>0.0000508</td>
<td>33.0</td>
<td>0.499</td>
</tr>
<tr>
<td>1331.0</td>
<td>0.0097</td>
<td>0.0000271</td>
<td>36.1</td>
<td>0.545</td>
</tr>
<tr>
<td>2662.0</td>
<td>0.0048</td>
<td>0.0000149</td>
<td>39.7</td>
<td>0.599</td>
</tr>
<tr>
<td>5324.0</td>
<td>0.0024</td>
<td>0.0000080</td>
<td>42.8</td>
<td>0.646</td>
</tr>
<tr>
<td>10648.0</td>
<td>0.0012</td>
<td>0.0000043</td>
<td>45.8</td>
<td>0.691</td>
</tr>
<tr>
<td>( \eta_{\infty} = 56.2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Ethyl Alcohol–Potassium Nitrate 30°**

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp. K.</th>
<th>( \eta )</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>309.5</td>
<td>0.0418</td>
<td>0.0001038</td>
<td>29.8</td>
<td>0.327</td>
</tr>
<tr>
<td>619.0</td>
<td>0.0209</td>
<td>0.0000546</td>
<td>33.8</td>
<td>0.372</td>
</tr>
<tr>
<td>1238.0</td>
<td>0.0104</td>
<td>0.0000306</td>
<td>37.9</td>
<td>0.416</td>
</tr>
<tr>
<td>2476.0</td>
<td>0.0052</td>
<td>0.0000170</td>
<td>42.2</td>
<td>0.464</td>
</tr>
<tr>
<td>4952.0</td>
<td>0.0026</td>
<td>0.0000095</td>
<td>47.2</td>
<td>0.519</td>
</tr>
<tr>
<td>9904.0</td>
<td>0.0013</td>
<td>0.0000053</td>
<td>52.1</td>
<td>0.573</td>
</tr>
<tr>
<td>( \eta_{\infty} = 90.9 )</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Ethyl Alcohol–Potassium Nitrate 35°**

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp. K.</th>
<th>( \eta )</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>290.5</td>
<td>0.0448</td>
<td>0.0001099</td>
<td>31.9</td>
<td>0.265</td>
</tr>
<tr>
<td>581.0</td>
<td>0.0224</td>
<td>0.0000627</td>
<td>36.5</td>
<td>0.303</td>
</tr>
<tr>
<td>1162.0</td>
<td>0.0112</td>
<td>0.0000357</td>
<td>41.5</td>
<td>0.344</td>
</tr>
<tr>
<td>2324.0</td>
<td>0.0056</td>
<td>0.0000203</td>
<td>47.2</td>
<td>0.392</td>
</tr>
<tr>
<td>4648.0</td>
<td>0.0028</td>
<td>0.0000113</td>
<td>52.3</td>
<td>0.434</td>
</tr>
<tr>
<td>9296.0</td>
<td>0.0014</td>
<td>0.0000063</td>
<td>58.5</td>
<td>0.485</td>
</tr>
<tr>
<td>( \eta_{\infty} = 120.5 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Propyl Alcohol—Potassium Chloride 25°

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp. K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1308</td>
<td>0.0071</td>
<td>0.00001187</td>
</tr>
<tr>
<td>2616</td>
<td>0.0036</td>
<td>0.00000690</td>
</tr>
<tr>
<td>5232</td>
<td>0.0018</td>
<td>0.00000390</td>
</tr>
<tr>
<td>10464</td>
<td>0.0009</td>
<td>0.00000237</td>
</tr>
</tbody>
</table>

### Propyl Alcohol—Potassium Nitrate 25°

<table>
<thead>
<tr>
<th>V</th>
<th>C</th>
<th>Sp. K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1340</td>
<td>0.0094</td>
<td>0.0000100</td>
</tr>
<tr>
<td>2680</td>
<td>0.0047</td>
<td>0.0000060</td>
</tr>
<tr>
<td>5360</td>
<td>0.0023</td>
<td>0.0000033</td>
</tr>
<tr>
<td>10720</td>
<td>0.0012</td>
<td>0.0000018</td>
</tr>
</tbody>
</table>
METHYL ALCOHOL
POTASSIUM CHLORIDE
25°
Potassium Chloride
Methyl Alcohol

(\(\text{KC}_2\))

30°

MISSOURI SCHOOL OF MINES
MISCHURE SCHOOL OF MINES

$\frac{1}{\mu}$

$0.01480$ $6.32$

$0.01332$ $5.19$

$0.01200$ $4.28$

$0.01094$ $3.43$

$0.00860$ $\mu$-constant $186.7$

METHYL ALCOHOL

POTASSIUM NITRATE

25°C

$(\theta_{1/2})^{33}$
Methyl Alcohol
Potassium Nitrate
30°
\[ \frac{1}{\mu} = 0.0047 \quad \mu = 213.0 \]

Methyl Alcohol
Potassium Nitrate
35°
Ethyl Alcohol
Potassium Chloride
25°
Ethyl Alcohol

Potassium Chloride

$(\text{C}_2\text{H}_5)_3\text{K}$

$30^\circ$
$\frac{1}{\mu} \left( \frac{C}{\mu} \right)^{33} = 0.0076 \quad \mu = 128.2$
$\frac{1}{\mu} \text{ vs. } (C/\mu)^{33}$

$\frac{1}{\mu} = 0.0156 \quad \mu = 66.2$

**Ethyl Alcohol**

**Potassium Nitrate**

$25^\circ$
Ethyl Alcohol
Potassium Nitrate
30°
\[ \frac{1}{\mu} \left( \frac{C}{\mu} \right)^{33} \]

**Ethyl Alcohol**

**Potassium Nitrate**

35°
DISCUSSION

One of the most striking observations one makes in connection with the study of the conductivities of alcoholic solutions is their great similarity to those of aqueous solutions with the exception that the values of the concentrations are very much smaller. The differences are rather of degree than of kind. It will be noted that as the temperature is increased the molecular conductivity increases and the fraction of salt decreases which is what would be expected by analogy.

The values of the molecular conductivity at infinite dilution are somewhat higher than was expected although their value, running lower than the corresponding value in water, seems not unreasonable when compared with some of the results obtained by earlier investigators. Jones obtained the value 124.0 in the case of cobalt bromide in ethyl alcohol at 25° and 144.6 in the case of cobalt chloride in methyl alcohol at 25° and a dilution of one mol in 1600 liters. The latter figure is not the limiting value which would of course be considerably higher.

In the case of the limiting values of potassium nitrate in methyl alcohol, however, it is somewhat
different, not so much on account of their magnitude as because of the fact that they are larger than the corresponding values of potassium chloride in methyl alcohol. For this reason there may be some cause to believe that the conductivity curve departs from a straight line curve at higher dilutions. Another possibility is that the platinized electrodes absorbed a certain amount of the salt when in contact with the stronger solutions and then when filled with the more dilute solutions allowed some of the salt to go back into solution thus raising the conductivity values all along the line. For this reason it would probably have been better to have measured the conductivities of the more dilute solutions first.

While discussing the question of absorption, the behavior of potassium sulphate must be mentioned. The conductivity of solutions of this salt in both alcohols was determined at three temperatures in the same way as were potassium chloride and nitrate but such discordant results were obtained that these values have been omitted from the data sheets. One or two sets of these readings, however, will be given.

In the case of potassium sulphate in methyl alcohol at 30° the following incongruous results were obtained for the specific conductivity:
In accounting for these values, two possibilities suggest themselves – the occurrence of a secondary ionization which had not attained equilibrium and absorption. The first possibility, it seems, may be dismissed, although the salt undoubtedly ionizes in this way, and the phenomenon attributed to absorption. This explanation seems probable as the values in the duplicate determination are higher than those in the first set of readings. A clearer case of absorption was found in the case of potassium sulphate in ethyl alcohol at 25°. The values for \( k \) are:

<table>
<thead>
<tr>
<th>( k )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000669</td>
<td>0.0000670</td>
</tr>
<tr>
<td>0.0000428</td>
<td>0.0000568</td>
</tr>
<tr>
<td>0.0000300</td>
<td>0.0000358</td>
</tr>
<tr>
<td>0.0000236</td>
<td>0.0000238</td>
</tr>
<tr>
<td>0.0000189</td>
<td>0.0000222</td>
</tr>
<tr>
<td>0.0000189</td>
<td>0.0000220</td>
</tr>
</tbody>
</table>

Each reading was taken at twice the dilution of the preceding one.
Here the values remain practically constant at all dilutions becoming only very slightly less as the dilution was increased. After this determination had been made it was necessary to clean the cell with cleaning solution and live steam before again putting it in to use.

On account of the small amount of propyl alcohol available, only one set of readings was taken using this solvent. As would be expected from the nature of this alcohol, the specific and molecular conductivities run considerably lower than in methyl and ethyl alcohols. On account of the limited data taken, no attempt was made to compute the ionization values.

The whole question of conductivity and ionization in alcoholic solutions is intimately bound up with the relation of conductivity, viscosity, and dielectric constant, and it is to be regretted that these values and their relations could not have been incorporated within this paper.

The dielectric constant of a solvent determines the force with which electric charges will attract and repel one another and, therefore, the higher the dielectric constant of a solvent the smaller will be the attraction of oppositely charged particles. Hence, in solvents having high dielectric constants, ionization is more favored than in solvents of
low dielectric powers.

The dielectric constant of water is 81, of methyl alcohol 32, and of ethyl alcohol 22. We would expect a salt to be more highly ionized in methyl alcohol than in ethyl alcohol and still more highly ionized in water than in methyl alcohol and such was found to be the case.

Another element to be taken into consideration is the part which the viscosity of the solution plays. A viscous, poorly conducting solution may contain the dissolved electrolyte in a highly ionized state while a thin, less viscous solution having only a small fraction of the electrolyte ionized may be a much better conductor due to the fact that the frictional resistance offered the ions is smaller. Considerable work has been done on this phase of the subject. Viscosity values on the solutions studied would undoubtedly suggest many interesting possibilities.

There is considerable evidence to support the assumption that methyl alcohol is associated to some extent and in a full explanation of the conductivity of alcoholic solutions, account will have to be taken of this phenomenon as well as of the viscosity and dielectric constant. The investigation of the influenza
of the association of the solvent and the relation between conductivity, viscosity, ionization, and dielectric constant, not only of alcohols, which have been pretty thoroughly investigated, but also of certain organic solvents of low dielectric constants such as benzene and ether, would certainly prove a most interesting problem.
SUMMARY

1. Methyl alcohol having a specific conductivity of $1.03 \times 10^{-6}$ and ethyl alcohol having a specific conductivity of $2 \times 10^{-7}$ have been prepared.

2. The values of the molecular conductivity at various concentrations and at infinite dilution of potassium chloride and potassium nitrate in methyl alcohol and ethyl alcohol have been determined.

3. The fraction of potassium chloride and potassium nitrate ionized in methyl alcohol and ethyl alcohol has been determined.

4. Platinized electrodes show absorptive power when used in certain alcoholic solutions.
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INDEX

A

Absorption, 44
Alcohol, dehydration of, 19
    -- Specific conductivity of, 49
Aluminum amalgam, 18
Amplifier, 12
Apparatus, mixing, 14

B

Bibliography, 50
Bridge, 12
    -- Wiring diagram for, 16

C

Cell constant, 21
Circuit, description of, 15
    -- Wiring diagram for, 16
Conductivity, specific, 26
    -- Molecular, 26
    -- at infinite dilution, 31
Conductivity cell, 14
Data, 25
Diagram, wiring
  --- for amplifier, 13
  --- for bridge, 16
Discussion, 43

Electrodes, 23, 44

Graphs, 31

History, 4

Ionization, 25
  --- secondary, 45
L
Lime, preparation of, 18

M
Microphone hummer, 12

P
Polarization, 15
Procedure, method of, 23

R
Resistance, 12

S
Salts, purification of, 18
Shielding, electromagnetic, 17
Summary, 49

T
Telephones, 14
Thermostat, 14
Water, conductivity, 20

The End