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CONDUCTIVITY AND NEGATIVE VISCOSITY COEFFICIENTS OF CERTAIN RUBIDIUM AND ALMONIUM SALTS IN GLYCEROL AND IN MIXTURES OF GLYCEROL WITH WATER

FROM 25° TO 75°

DISSERTATION.

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

- by-

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TABLE OF CONTENTS.

Acknowledgment	• C
Introduction	. 1
Glycerol as a solvent	. 4

m, 1

EXPERIMENTAL.

Apparatus	• • • • •	• • •	
Solutions	• • • • •	•••	
Solvents		•••	
Salts	• • • • •	• • •	
Procedure	• • • • •	•••	l
Conductivity	Data	in	Glycerol 19
79	"	11	Glycerol-water mixtures 29

Comparison of Temperature Coefficients	37
Viscosities and Fluidities in Glycerol	38
Viscosities and Fluidities in mixed sorvents	4 8
Per cent increase in Fluidities	56

DISCUSSION OF RESULTS.

Conductivity	57
Negative Viscosity	61
Conductivity Minima and Negative Viscosity	63
Per cent coefficients of Fluidity	65
Summary	66
Biography	68

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Special thanks are due to Professor Jones, at whose suggestion and under whose direction this investigation was carried out.

The author also feels under obligation to Drs. Guy and Wightman for kindly advice and assistance.

INTRODUCTION.

The work of Jones and seven of his collaborators, viz., Lindsay,¹ Carroll,² Bassett,³ Bingham,⁴ Rouiller,⁵ McMaster,⁶ and Veasey⁷ on the relations between the conductivity and viscosity of electrolytes in various organic solvents and in binary mixtures of these, has been fully discussed in Monograph No. 80 of the Carnegie Institution of Washington.

In addition to this Jones and Schmidt⁸ have given a complete historical sketch of all the work in mixed solvents including that which followed the publication of the above mentioned monograph. This covered the work carried out by Mahin⁹ and by Kreider.¹⁰ In both of these communications due credit has been given to previous workers in this field. Therefore, to avoid unnecessary repetition, discussion of their results will be taken up only in so far as they bear directly on this investigation.

(1) Amer. Chem. J., 28, 329 (1902). (2) Ibid 32, 521 (1904). (3) Ibid 32,409 (1904). (4) Ibid 34, 481 (1905). (5) Ibid 36, 427 (1906). (6) Ibid 36, 325 (1906). (7) Zeit. f. Phys. Chem., 61, 64 (1908). (8) Amer. Chem. J., 42, 37 (1909). (9) Zeit. f. Phys. Chem. 69, 389 (1909). (10) Amer. Chem. J. 45, 295 (1911).

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The first of these investigators in this laboratory to note the phenomenon of negative viscosity was Vcazey.¹ He measured the conductivity and viscosity of potassium sulfocyanate in water, ethyl and methyl alcohols, and acetone and in binary mixtures of these solvents. In water and in certain mixtures of the alcohols with water he noted a marked negative viscosity.

Prior to Veazey's investigation, Euler ² had attempted to explain the lowering of the viscosity of a solvent by a discolved substance on the basis of the "electrostriction" of the solvent caused by the charge upon the ions of the solute as proposed by Drude and Nernst. ³

But Wagner and Muhlenbein ⁴ showed that Euler's explanation was not valid since cortain non-electrolytes in organic solvents also show negative viscosity, c.g., cyanobenzol in ethyl alcohol.

The explanation offered by Jones and Veazey is based on their own observations and on the classical work of Thorpe and Roger. ⁵ The latter have indicated that visecsity phenomena are in all probability dependent upon the frictional surfaces of the ultimate particles present in any liquid or solution. A review of the data obtained

(1) Amer. Chem. J., 37, 405 (1907).
 (2) Zeit. f. Phys. Chem. 25, 556 (1898).
 (3) Ibid, 15, 79 (1894).
 (4) Ibid, 46, 867 (1903).
 (5) Phil. Trans., 185-A, 307 (1894).

by Wagner ¹ from his study of the viscosity of a number of inorganic salts in water will show that he found negative viscosity only in the case of caesium rubidium and potassium salts -- and in some instances thallous salts. The first three metals occupy the maxima on the atomic volume work of Lothar Meyer, ² i.e., they have the largest atomic volumes of the elements. That some salts of potassium gave positive viscosity is to be expected since it has been shown that viscosity is an additive function of both the cation and the anion of the dissolved salt. In the case in question, the one might tend to lower the viscosity of the solvent, the other to increase it, the final rosults depending upon whether the sum of these two opposing forces was positive or negative. Potassium has the smallest atomic volume of the three and in many instances the positive viscosity effect of the anion would entirely overcome the negative effect of the cation.

In view of these facts, Jones and Veazey offered the apparently satisfactory explanation that "negative viscosity" is due to a lessening of the skin friction between the solvent and the molecules or ions of a solute because of the large atomic volume of the cations as compared with the molecular aggregates of the solvent. This explanation follows directly from the work of Thorpe and Roger.

(1) Zeit. f. Phys. Chem., 15, 31 (1890).
(2) Ann. Chem. (Liebig), Suppl., 7, 354 (1870).

W. Taylor ¹ measured the viscosity of one, two and three molar solutions of potassium chloride, bromide and iodide in water at different temperatures and noted that negative viscosity may pass over into positive viscosity with rise in temperature and confirmed the view that viscosity depends upon the nature of both cation and anion. He noted also the negative viscosity effect of ammonium iodide when dissolved in water.

Reference should be made to the extensive work of Walden 2 on the relations that exist between viscosity and conductivity at infinite dilutions. He finds that Moo Moo = 0 for more than thirty organic solvents.

Exceptions have been noted to this relationship and these will be taken up later.

Glycerol as a solvent. - An examination of the literature bearing on this problem shows that only a little work had been done previous to that of Jones and Schmidt.

Cattaneo³ measured the conductivity of several halides of the metals in glycerol and noted that the values obtained were much smaller than the corresponding values in water or alcohol.

(1) Edin Proc. 25, 227 (1904) and Edin Trans 45, 397 (1906).
(2) Zeit. f. Phys. Chem. 78, 257 (1911).

(3) Rend. R. Accad. Lincei., (5) 2, II, 112 (1893).

Schottner ¹ measured the viscosity of certain mixtures of glycerol and water. Arrhenius ² studied the viscosity of mixtures of various organic substances with water, among them glycerol, and noted that the temperature coefficients of viscosity were greatest where the viscosity was greatest.

Schall and Van Rijn ³ determined the relative viscosities of mixtures of glycerol with water and alcohol.

Lemke ⁴ carried out an investigation on the conductivity and viscosity of water glycerol mixtures at 25⁰ and was led to conclude that ionization and hence electrical conductivity is proportional to the viscosity of the solvent as well as to the association. He noted the periodic viscosity of sodium chloride in 9.8 percent glycerol and water and a negative viscosity in water at certain dilutions.

Getman ⁵ studied the viscosity of potassium iodide in various organic solvents including glycerol and noted negative viscosity <u>only</u> in the case of the latter. This he attributed to the association of the solvent.

Jones and Schmidt⁶ have studied the conductivity of lithium bromide, cobalt chloride and potassium iodide

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    Wien. Ber. 77, II. 682 (1878).
    Z. f. Phys. Chem. I, 285 (1887).
    Ibid 23, 329 (1897).
    Zeit. f. Phys. Chem. 52, 479 (1905).
    J. Amer. Chem. Soc. 30, 1077 (1908).
    Loc. cit.
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in glycerol at 25° , 35° and 45° , and in mixtures of glycerol with water with ethyl alcohol and with methyl alcohol at 25° and 35° . Measurements of viscosity were also made with the N/10 solution in the various solvents. They have shown that glycerol is an excellent solvent and in all probability a comparatively good dissociant since it has a dielectric constant of 16.5 at 18° and an association factor of 1.8 at that temperature. From this data glycerol according to the Thompson,¹ Nernst ² and Dutcit and Aston ³ hypothesis should have a dissociating power close to that of ethyl alcohol. The extremely low conductivity values obtained were attributed to the high viscosity of the solvent.

Schmidt noted that all the salts studied increased the viscosity of glycerol in N/10 solutions but that XI lowered the viscosity of water, and of 25 and 50 percent glycerol with water at 25° and 35° . He also showed that the effect of the several salts studied on the viscosity of glycerol was in inverse ratio to the atomic volume of the cations exactly analogous to the observations of Jones and Veazey in aqueous solutions. Schmidt also found glycerol to be an apparent exception to the observations of Walden, ⁴ previously mentioned, that $\mathcal{M}_{\infty}\mathcal{M}_{\infty} = 0$. Further

(1) Phil. Mag. 36, 320 (1893).

(2) Zeit. f. Phys. Chem. 13, 531 (1894).

(3) Compt. Rend. 125, 240 (1897).

(4) Zeits. f. Phys. Chem. 55, 246ff (1906) and 78, 257 (1911).

exceptions in the case of water and glycol have been noted by Walden from his own investigations.

The most extensive investigation of glycerol as a solvent has recently been carried out by Jones and Guy! They took up the behavior of some twenty electrolytes in pure glycerol and in binary mixtures of glycerol with ethyl alcohol, with methyl alcohol and with water at intervals of ten degrees from 25° to 75° for the pure solvent and from 25° to 45° in mixed solvents. Conductivity measurements were made over a range of V = 10 to V = 1600 and viscosity measurements with the N/10 solutions. They find that the molecular conductivities in glycerol are all extremely small but show a regular increase with increased dilution and rise in temperature. Furthermore a study of the temperature coefficients brought out the fact that in the case of those salts that have been shown to have large hydrating power in water, such as salts of barium strontium, calcium and cobalt, the relative increase was larger than with salts of sodium potassium and ammonium which show little or no hydrating power in aqueous solutions. Here we have evidence of solvation in glycerol supporting that obtained by Jones and Strong 2 from spectroscopic methods.

In mixed solvents, Jones and Guy studied salts of (1) Amer. Chem. J., 46, 131 (1911).

(2) Monographs Nos. 130 and 160, Carnegie Institution of Washington.

potassium, sodium, ammonium and strontium in various mixtures of glycerol with water and with ethyl and methyl alcohols. They find that conductivities in such mixtures do not follow the law of averages but are always lower. This they explain by the facts established by Jones and Murray ¹ and Jones and Lindsay ² that two highly associated solvents when mixed tend to break down the association each of the other and hence their combined power of dissociating electrolytes is less than if there were no mutual lowering of their association, i.e., if each solvent acted independently of the other.

From the viscosity data Guy has shown that the temperature coefficients of fluidity in pure glycerol are very large and nearly equal to those of conductivity. Also that the ternaryelectrolytes studied increased the viscosity of glycerol to a much greater extent than the binary electrolytes. This is attributed to the smaller atomic volumes of barium, strontium, calcium and cobalt and to the solvation of the molecules of the solute. In mixed solvents the curves representing conductivity and fluidity were found to be strikingly analogous.

Probably the most interesting point brought out by Guy was the large viscosity lowering observed in the case (1) Amer. Chem. J., 30, 193 (1903). (2) Ibid 28, 329, 1902.

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of certain salts in pure glycerol, e.g., N/10 solutions of sodium nitrate, ammonium bromide, ammonium iodide and rubidium bromide. The explanation of this phenomena is derived from that of Jones and Veazey¹ for similar salts in water. This fact suggested the closer study of some of these salts over a wider range of concentration, the present investigation being a continuation of the work of Jones and Schmidt and Jones and Guy.

Work on this problem was begun in collaboration with Wm. A. A. Reinhardt, A.B., of Baltimore, a graduate of this university, whose untimely and lamentable death in September of last year proved a serious set back to the carrying out of the investigation. The writer wishes to pay tribute here to his friend and coworker as an earnest, sincere student, one who was rapidly coming to the front among the research students in this laboratory.

The conductivity data on ammonium iodide in mixed solvents obtained by Mr. Reinhardt are incorporated in this paper.

(1) Loc. Cit.

Apparatus.

The constant temperature baths used in this investigation were of the form usually employed for such work in this laboratory. The thermostat for viscosity measurements was provided with glass windows, both front and rear, to facilitate the reading of the viscosimeters. Both baths were equipped with cooling coils in which the water was maintained at constant pressure. This facilitated temperature regulation below 35° . A closely fitting cover was provided for the conductivity bath for work above 35° , to prevent steaming and to maintain the air immediately above the cells at as near as possible the temperature of the water in the bath.

The temperature of the thermostats was maintained constant to within 0.02° by means of electrically controlled gas regulators devised by Reid.¹ The thermometer used in the conductivity bath was of the usual 100° enclosed scale type, graduated in 0.1° and could be read to .02° with a hand lens. For work up to 45° the viscosity bath was provided with a 25° Beckmann thermometer graduated to 0.05° and with a certified Bender and Hobein thermometer for higher temperatures. All thermometers were first standardized against a certified Reichsanstalt instrument

(1) Amer. Chem. J., 41, 148 (1909).

and comparisons were frequently made during the course of the work.

The conductivity apparatus consisted of the usual Kohlrausch slide wire bridge, resistance box, induction coil and telephone receiver. This apparatus was made and standardized by Leeds and Northrup of Philadelphia and in addition the resistances were compared with a rheostat which had been standardized by the Bureau of Standards, Washington, D.C. The bridge wire was calibrated as directed by Jones ¹ and found to be of uniform resistance thruout. Under favorable conditions separate readings with the same resistance agreed with one another to one half of a millimeter, the nature of the solvent preventing closer agreements.

The conductivity cells used were of two types, those of the ordinary plate type as described by Bingham,² had constants ranging from 40 to 339 and were used with the mere concentrated solutions. For the N/10 to N/1600 solutions, five cells of the type previously described by Jones and Schmidt,³ and Jones and Kreider⁴ were used. Their constants ranged from 2.35 to 4.36, and because of this they were well adapted to the measurement of high resistances.

- (1) Freezing Point Boiling-point and Conductivity Methods.
- (2) Loc. cit.
- (3) Loc. cit.
- (4) Loc. cit.

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Cell constants were determined with a fiftieth normal potassium chloride solution as a basis, this being diluted to five-hundredth and two-thousandth normal for the low constant cells. Checks were made at regular intervals and showed only slight variations in the cell constants, especially in the case of the cells with concentric cylindrical electrodes.

The molecular conductivity of the fiftieth normal solution was taken as 129.7 reciprocal Siemens units, at 25°. That of the more dilute solutions was determined by direct measurements.

Viscosity measurements were made with the Ostwald viscosimeter ¹as modified by Jones and Veazey,² the size of the capillary being regulated to the solutions for which they were employed. The viscosimeters were calibrated as described by Schmidt,³ the time of flow for water in the instruments used for glycerol being derived from the formula:

$$f''_{w} = \frac{f'_{w} \cdot f'_{A} \cdot f''_{B}}{f'_{A} \cdot f''_{B}}$$

where \neq'_{w} is the time of flow of water in the water viscosimeter, \neq'_{A} the time for a slightly more viscous solution in the water viscosimeter; \neq''_{A} , \neq''_{B} and \neq'''_{B} the times of

- (1) Ostwald-Luther: Phys.-chem. Mess. 3rd Ed. (1910), p. 232.
- (2) Zeit. f. Phys. Chem. 61, 641 (1908).
- (3) Loc. cit.

12

flow of the solutions A and B of intermediate viscosities between water and glycerol in an intermediate viscosimeter and in the instrument for glycerol; $\not \sim''$ the derived time of flow in the glycerol viscosimeter. The viscosimeters were filled by means of carefully calibrated pipettes with such a volume of liquid as to fill them from the middle of the upper to the middle of the lower bulb. With such an arrangement, according to Appleby $\frac{1}{2}$ the alteration in hydrostatic pressure due to small variations in the volume of the liquid is a minimum.

On account of the steaming of the viscosity thermostat at high temperatures, the viscosimeters after filling were provided with a simple apparatus designed to exclude dust and moisture and to eliminate the danger of obstructing the free passage of the air from one arm of the viscosimeter to the other during the flow of the liquid through the capillary. This consisted of two T shaped guard tubes each provided with a small bulb in the long arm. These bulbs were filled with cotton wool to filter out dust particles. One end of the cross arm of a guard tube was connected to each arm of the viscosimeter and the opposite ends joined by a short length of rubber tubing. The liquid was drawn up in the capillary arm of the viscosimeter by compressing the rubber tube and attaching the bulb arm of the guard tube on that side to an aspirator, the air entering through the guard tube on the opposite (reservoir) arm is thoroughly

(1) J. Chem. Soc., 972, 2000 (1910).

dried by passing over calcium chloride and freed from dust by the cotton wool mentioned above. When the liquid has risen to a point slightly above the upper mark on the viscosimeter the compression on the rubber tube is released and the air pressure immediately equalizes itself on both sides of the viscosimeter. By this arrangement no air from the outside enters during the actual flow of the liquid through the capillary.

Viscosimeters, while being read, were supported in the bath by means of special clamps with cork lined jaws attached to a heavy stand which was carefully leveled.

Specific gravity determinations were made by means of the Ostwald pycnometer as modified for liquids with large expansion by Jones and Veazey.¹

All measuring flasks and pipettes were carefully calibrated either by direct weighing or by the method of Morse and Blalock² to hold aliquot parts of the true liter at 20° , and solutions were brought to within 0.1° of this temperature before being diluted to the mark.

Solutions.

Because of a limited supply of salts at hand all solutions were made up at 20° and a temperature correction made (1) Loc. Cit.

(2) Amer. Chem. J., 16, 479 (1904).

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for temperatures above 25°. The expansion coefficient for glycerol was taken as .00049 and was determined from specific gravity measurements in the viscosity work.

Solutions of the N, 3/4 N, N/2, N/4 and 1/10 normal were made by direct weighing of the anhydrous salt which had been previously dried for some time in an air bath at $130^{\circ}-135^{\circ}$.From the 1/10 normal solution the N/50 and N/100solutions were made by dilution. These in turn served as mother solutions for the N/200 and N/400 from which the N/800 and N/1600 solutions were made in a similar manner. The latter was made by diluting the N/400 solution four times.

Because of the hydroscopic nature of the solvent and the difficulty in obtaining proper drainage of burettes containing it, measuring flasks were used exclusively in the dilution of solutions in glycerol. In every case the proper measuring flask was filled with the mother solution, set in a thermostat at 20°, warmed in an air bath to 70°-80°, drained as quickly as possible with the receiving flask, then washed out at least three times with the warmed solvent. The flask containing the more dilute solution was then filled up nearly to the neck with the solvent warmed and shaken thoroughly without wetting the neck, then filled to a point slightly above the mark and finally set after cooling to 20° in a thermostat. Final warming in the air bath and thorough shaking completed the operation. The flasks used were of Jena Normal glass, eliminating as far

as possible the danger of the action of the solvent on the glass. Some time was allowed before the final dilution to the mark to permit the glass to contract properly after the unavoidable heating during the process of dilution.

On account of the extremely high resistance offered by glycerol solutions conductivity measurements were not made at dilutions greater than N/1600. Even at that dilution considerable difficulty was experienced in obtaining concordant readings. As an example it might be well to note that N/1600 solutions in glycerol in a cell with a constant as low as 2.3 required a balancing resistance of from 8,000 to 10,000 ohms while pure glycerol in the same cell required 20,000 to 22,000 ohms.

Conductivity and viscosity measurements in pure glycerol were made at intervals of ten degrees from 20° to 75° and in glycerol-water mixtures at 25° , 35°, and 45° . Viscosity measurements were not made at a greater dilution than N/10 since at lower concentrations γ approaches γ_{∞} too closely to be accurately differentiated.

Solvents.

<u>Glycerol</u>.- The glycerol used was from a new lot of Kahlbaum's "Doppelt - Dist. 1.26" and had a mean specific conductivity of about 0.6 x 10^{-7} at 25° and a mean specific gravity of 1.257 at the same temperature. No attempt was made to redistill it, since Schmidt had already shown that redistillation did not appreciably lower the conductivity.

<u>Water</u>. The water was purified by the method of Jones and Mackay¹ with the improvement as mentioned by Schmidt² and had a mean specific conductivity of $1.5-2 \times 10^{-6}$ at 25° .

Salts.

The Rubidium and Ammonium salts used in this work were from Fahlbaum's best products. These were recrystallized two or three times from conductivity water and carefully dried each time at 130-135° before weighing. In addition the rubidium salts were examined spectroscopically and showed the presence of only traces of sodium and no potassium. The ammonium iodide was pure white after drying and solutions of it in glycerol were only slightly tinted after standing some time.

Procedure.

Conductivity data was calculated in the usual way.

Viscosity measurements were calculated from the formula

$$\frac{\eta}{\eta_o} = \frac{St}{S_o t_o}$$

in which is the viscosity coefficient for the liquid in question, the absolute viscosity of water, S the specific gravity of the liquid at the given temperature, (1) Amer. Chem. J. 1783 (1895). (2) Loc. Cit.

t the time of flow of the same, S_0 and to the density and time of flow of water at the same temperature.

Fluidity was calculated from the formula

$$\phi = \frac{1}{2}$$

where ϕ represents the fluidity.

The absolute viscosities of water as given by Thorpe and Roger¹ are

25°	0.00891		0.005055
	0.00720		0.004355
45^{0}	0.00597	75 ⁰	0.003795

<u>Temperature coefficients.</u> The temperature coefficients in conductivity units represent simply the actual increase in conductivity per degree rise in temperature.

Percent. temperature coefficients, both of conductivity and fluidity, were calculated from the formula

Temp. coeff. of $(\mathcal{U}_V, \varphi) = \frac{1}{(\mathcal{U}_V, \varphi)25^\circ} \frac{(\mathcal{U}_V, \varphi)35^\circ - (\mathcal{U}_V, \varphi)25^\circ}{10}$

An attempt was made to obtain conductivity and viscosity data on the sulfate of rubidium, but it was not possible to obtain a solution of higher concentration than N/200.

It was originally intended to carry on a parallel investigation with caesium salts, but we have been thus far unable to secure sufficient quantities for the work. (1) Loc. Cit.

	<u>Glycerol at 250</u>	$, 35^{\circ}, 45^{\circ}.$	
v	M, 250	, 1, 35°	//. 45°
1.0	0.389	0.770	1.385
1.3	0.371	0.746	1.361
2.0	0.348	0.717	1.312
4.0	0.326	0.665	1.224
10	0.342	0.700	1.321
50	0.359	0.740	1.373
100	0.369	0.764	1.414
200	0.365	0.760	1.396
400	0.371	0.753	1.401
800	0.404	0.777	$1.441 \\ 1.457$
1600	0.413	0.811	

TABLE II	Temperature	Coefficients.
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Per Cent.

v				
	25°-35°	35°-45°	250_350	35 ⁰ -45 ⁰
l	0.0979	0.0799	0.0381	0.0615
1.3	0.1012	0.0824	0.0375	0.0615
2	0.1060	0.0830	0.0369	0.0595
4	0.1040	0.0841	0.0339	0.0559
10	0.1047	0.0887	0.0358	0.0621
50	0.1061	0.0855	0.0381	0.0633
100	0.1070	0.0851	0.0395	0.0650
200	0.1082	0.0837	0.0395	0.0636
400	0.1030	0.0860	0.0382	0.0648
800	0.0923	0.0854	0.0373	0.0664
1600	0.0964	0.0797	0.0398	0.0646

TUDIO TIT.	Morecular co	Inductivity of Annio	nium iouide in
	<u>Glycerol at</u>	$55^{\circ}, 65^{\circ}, 75^{\circ}.$	
A	N: 55°	65°	/1, 750
1.0	2.304	3.602	5.260
1.3	2.268	3.540	5.189
2.0	2.140	3.404	5.072
4.0	2.069	3.266	4.858
10	2.210	3.506	5.278
50	2.331	3.707	5.534
100	2.424	3.843	5.772
200	2.386	3.805	5.606
400	2.410	3.819	5.749
800	2.485	4.010	5.950
1600	2.528	4.130	6.100

TABLE III. - Molecular Conductivity of Ammonium Iodide in

TABLE	IV.	-	Temperature	Coefficients.

Per Cent.

v	45°-55°	55 ⁰ -65 ⁰	650-750	45°-55°	55 ⁰ -65 ⁰	650_750
1 1.3 2 4 10 50 100 200 400 800	0.0663 0.0666 0.0631 0.0690 0.0673 0.0698 0.0714 0.0709 0.0720 0.0724	0.0563 0.0561 0.0591 0.0578 0.0586 0.0590 0.0585 0.0590 0.0585	$\begin{array}{c} 0.0460\\ 0.0466\\ 0.0490\\ 0.0487\\ 0.0505\\ 0.0493\\ 0.0476\\ 0.0473\\ 0.0473\\ 0.0505\\ 0.0484\end{array}$	0.0919 0.0907 0.0828 0.0845 0.0889 0.0958 0.1010 0.0990 0.1009 0.1044	0.1298 0.1272 0.1264 0.1197 0.1296 0.1296 0.1376 0.1419 0.1419 0.1409 0.1525	0.1658 0.1649 0.1668 0.1592 0.1772 0.1827 0.1829 0.1801 0.1930 0.1940
1600	0.0735	0.0634	0.0477	0.1071	0.1602	0.1970

TABLE V	- Molecular Conduc	tivity of Rubidiu	um Chloride
	in <u>Glycerol</u> at 2	$25^{\circ}, 35^{\circ}, 45^{\circ}.$	
v	/1 25 ⁰	, i', 35 ⁰	45°
l.	0.374	0.738	1.320
1.3	0.371	0.740	1.337
2	0.386	0.767	1.371
4	0.376	0.771	1.390
10	0.380	0.771	1.410
50	0.401	0.819	1.502
100	0.420	0.848	1.563
200	0.428	0.860	1.588
400	0.432	0.887	1.633
800	0.444	0.874	1.625
1600	0.448	0.892	1.643

TABLE VI.	-	Temperature	Coefficients.

Per Cent.

v	25 ⁰ -35 ⁰	35°-45°	25°-35°	35 [°] -45 [°]
1. 1.3 2. 4 10 50 100 200 400 800 1600	0.0973 0.0995 0.0987 0.1050 0.1029 0.1042 0.1019 0.1009 0.1053 0.0970 0.0991	0.0789 0.0807 0.0812 0.0784 0.0829 0.0834 0.0843 0.0843 0.0841 0.0859 0.0842	0.0364 0.0369 0.0381 0.0395 0.0391 0.0418 0.0428 0.0428 0.0432 0.0432 0.0435 0.0430 0.0444	0.0582 0.0597 0.0623 0.0604 0.0639 0.0683 0.0715 0.0728 0.0746 0.0751 0.0751

	in Glycerol at	35° , 65° , 75° .	
V	Mv 55 ⁰	. Liz 650	(, 750
1.	2.205	3.400	4.994
1.3	2.215	3.421	5.014
2	2.307	3.570	5.272
4	2.310	3.585	5.382
10	2.386	3.749	5.684
50	2.561	4.003	6.041
100	2.649	4.180	6.343
200	2.720	4.282	6.408
400	2.784	4.408	6.542
800	2.774	4.358	6.532
1600	2.831	4.462	6.574

TABLE VII. - Molecular Conductivity of Rubidium Chloride

TABLE	VIII.	-	Temperature	Coefficients.
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P	e	r	Cent	
_	0	-		•

				·····	- Contraction of the second	
v	45°-55°	550-650	650_750	45°-55°	55 ⁰ -65 ⁰	65 ⁰ -75 ⁰
1.	0.0670	0.0542	0.0469	0.0885	C.1195	0.1594
1.3	0.0657	0.0544	0.0466	0.0878	0.1206	0.1593
2	0.0677	0.0547	0.0477	0.0936	0.1263	0.1702
4	0.0662	0.0553	0.0501	0.0920	0.1275	0.1797
10	0.0692	0.0571	0.0516	0.0976	0.1363	0.1935
50	0.0705	0.0563	0.0509	0.1059	0.1442	0.2038
100	0.0695	0.0578	0.0517	0.1086	0.1531	0.2163
200	0.0713	0.0574	0.0496	0.1132	0.1562	0.2126
400	0.0705	C.0547	0.0484	0.1151	0.1524	0.2134
800	C.0707	0.0571	0.0498	0.1149	0.1584	0.2174
1600	0.0723	0.0576	0.0473	0.1188	0.1631	0.2112

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TABLE IX		uctivity of Rubi 25°, 35°, 45°.	dium Bromide
v	1. 25°	×, 35°	450
1. 1.3 4 10 50 100 200 400 800 1600	0.368 0.360 0.363 0.369 0.379 0.409 0.427 0.427 0.451 0.470 0.480	C.717 .716 C.732 O.752 O.785 O.835 O.835 O.855 O.879 O.893 O.893	1.273 1.311 1.339 1.385 1.456 1.483 1.592 1.627 1.633 1.700

Per Cent.

Cond. Units.

	·····			
V	25 ⁰ -35 ⁰	35 ⁰ -45 ⁰	25°-35°	35 ⁰ -45 ⁰
1. 1.3 4 10 50 100 200 400 800 1600	0.0948 0.0989 0.1016 0.1037 0.1071 0.1057 0.1036 0.1011 0.1020 0.1198	0.0775 0.0831 0.0828 0.0842 0.0855 0.0776 0.0851 0.0851 0.0829 0.0824	0.0349 0.0356 0.0369 0.0383 0.0406 0.0429 0.0435 0.0442 0.0451 0.0508	0.0556 0.0595 0.0607 0.0633 0.0671 0.0648 0.0737 0.0748 0.0740 0.0768

TABLE XI. - Molecular Conductivity of Rubidium Bromide

in Glycerol at 55°, 65°, 75°.

v	/ _v 55 ⁰	65 ⁰	750
1. 1.3 4 10 50 100 200 400 800 1600	2.143 2.198 2.217 2.524 2.473 2.623 2.623 2.698 2.711 2.724 2.722	3.056 3.424 3.489 3.676 3.876 4.153 4.291 4.348 4.401 4.499	4.595 4.604 5.120 5.483 5.763 6.236 6.236 6.477 6.592 6.666 6.855

TABLE	XII.	-	Temperature	Coefficients.

Dana	Cent.
Per	Uent.
~ ~ .	+ 0 + + 0 +

Cond. Units.

٧	45°-55°	55 ⁰ -65 ⁰	65°-75°	45 [°] -55 [°]	55 ⁰ -65 ⁰	650_750
1. 1.3 4 10 50 100 200 400 800	0.0683 0.0677 0.0656 0.0678 0.0698 0.0769 0.0693 0.0650 0.0668	$\begin{array}{c} 0.0426 \\ 0.0558 \\ 0.0569 \\ 0.0580 \\ 0.0567 \\ 0.0583 \\ 0.0590 \\ 0.0604 \\ 0.0616 \\ 0.0616 \end{array}$	0.0504 0.0345 0.0318 0.0492 0.0487 0.0501 0.0509 0.0516 0.0515	0.0870 0.0887 0.0939 0.1017 0.1140 0.1104 0.1058 0.1091	0.0913 0.1226 0.1262 0.1352 0.1402 0.1530 0.1593 0.1637 0.1637	0.1539 0.1180 0.1631 0.1807 0.1887 0.2083 0.2186 0.2244 0.2244
4 10 50 100 200 400	0.0656 0.0678 0.0698 0.0769 0.0693 0.0650	0.0569 0.0580 0.0567 0.0583 0.0590 0.0604	0.0318 0.0492 0.0487 0.0501 0.0509 0.0516	0.0878 0.0939 0.1017 0.1140 0.1104 0.1058	0.1262 0.1352 0.1402 0.1530 0.1593 0.1637	0.1631 0.1807 0.1887 0.2083 0.2186 0.2244

TABLE XIII. - Molecular Conductivity of Rubidium Iodide

in Glycerol at 25°, 35°, 45°.

v	250	350	450
1.	0.355	0.704	1.275
1.33 2	$0.342 \\ 0.334$	0.688 0.680	1.252 1.236
$\tilde{4}$	0.321	0.649	1.212
10	0.323	0.657	1.213
50 100	0.345 0.356	0.703 0.721	1.330 1.361
200	0.363	0.745	1.373
400 800	0.368 0.370	0.751 0.781	1.391 1.380
1600	0.373	0.805	1.389

TABLE XIV. - Temperature Coefficients.

Per Cent.

1.0.09830.08100.031.330.10120.08190.032.0.10360.08180.03		-
1.33 0.1012 0.0819 0.03 2. 0.1036 0.0818 0.03	-35° 35°-45)
10 0.1034 0.0846 0.00	346 0.0564 346 0.0556 328 0.0563	
50 0.1038 0.0892 0.03 100 0.1025 0.0888 0.03 200 0.1052 0.0844 0.03 400 0.1041 0.0857 0.03 800 0.1110 0.0767 0.03 1600 0.0159 0.0725 0.04	365 0.0640 382 0.0628 383 0.0644 411 0.0599	

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TABLE XV.- Molecular Conductivity of Rubidium Iodide

in Glycerol at 55°, 65°, 75°.

v	/1. 55°	, tr. 65°	× 75 ⁰
1. 1.3 2. 4. 10 50 100 200 400	$\begin{array}{c} 2.111\\ 2.100\\ 2.089\\ 2.034\\ 2.007\\ 2.256\\ 2.320\\ 2.360\\ 2.408\\ \end{array}$	3.229 3.286 3.278 3.197 3.103 3.575 3.687 3.861 3.937	$\begin{array}{c} 4.771 \\ 4.812 \\ 4.829 \\ 4.703 \\ 4.667 \\ 5.408 \\ 5.466 \\ 5.743 \\ 5.832 \end{array}$
800 1600	2.405 2.395	3.941 4.150	5.756 5.809

TABLE XVI. - Temperature Coefficients.

Per Cent.

v	45 [°] -55 [°]	55 [°] -65 [°]	65 ⁰ -75 ⁰	45 [°] -55 [°]	55°-65°	65 ⁰ -75 ⁰
1.	0.0656	0.0530	0.0474	0.0836	0.1118	0.1542
1.3	0.0677	0.0565	0.0464	0.0848	0.1186	0.1526
2.	0.0690	0.0569	0.0473	0.0853	0.1189	0.1551
4.	0.0678	0.0572	0.0471	0.0822	0.1163	0.1506
10	0.0674	0.0546	0.0499	0.0794	0.1096	0.1564
50	0.0696	0.0584	0.0541	0.0926	0.1318	0.1833
100	0.0705	0.0588	0.0455	0.0960	0.1366	0.1779
200	0.0719	0.0636	0.0487	0.0987	0.1501	0.1882
400	0.0731	0.0635	0.0481	0.1017	0.1529	0.1895
800	0.0742	0.0628	0.0461	0.1025	0.1536	0.1815
1600	0.0724	0.0732	0.0402	0.1006	0.1755	0.1659

	in Glycerol	at 25° , 35° , 45° .	
v	25 ⁰	35 ⁰	45 ⁰
2	0.299	0.625	1.093
4	0.294	0.611	1.127
10	0.325	0.666	1.228
50	0.366	0.742	1.384
100	0.386	0.793	1.450
200	C.388	0.793	1.490
400	0.407	0.801	1.471
800	0.417	0.873	1.550

TABLE XVII. - Molecular Conductivity of Rubidium Nitrate

TABLE XVIII. - Temperature Coefficients.

Per Cent.

V	25 [°] -35 [°]	35 [°] -45 [°]	25 ⁰ -35 ⁰	35 ⁰ - 45 0
2 4 10 50 100 200 400	0.1090 0.1078 0.1046 0.1027 0.1051 0.1044 0.0968	0.0749 0.0844 0.0844 0.0965 0.0829 0.0879 0.0836	0.0326 0.0317 0.0341 0.0376 0.0407 0.0405 0.0394	0.0468 0.0516 0.0562 0.0642 0.0657 0.0697 0.0697
400 800	0.1096	0.0776	0.0456	0.0677

	in <u>Glycerol</u> at	55° , 65° , 75° .	
v	550	65 ⁰	750
2	1.930	3.005	4.435
4	1.913	2.979	4.392
10	2.088	3.272	4.866
50	2.350	3.712	5.570
100	2.481	3.917	5.894
200	2.495	4.000	5.960
400	2.487	3.932	5.862
800	2.605	4.161	6.174

TABLE XIX. - Molecular Conductivity of Rubidium Nitrate

TABLE XX. - <u>Temperature</u> <u>Coefficients</u>.

Per Cent. Cond. Units.

				and a second			
v	45 ⁰ -55 ⁰	55°-65°	65 ⁰ -75 ⁰	45 [°] -55 [°]	55 ⁰ -65 ⁰	65 ⁰ -75	
2	0.0763	0.0557	0.0475	0.0837	0.1075	0.1430	
4	0.0698	0.0557	0.0474	0.0786	0.1066	0.1413	
10	0.0700	0.0568	0.0487	0.0860	0.1184	0.1594	
50	0.0699	0.0579	0.0505	0.0966	0.1362	0.1858	
100	0.0710	0.0579	0.0505	0.1031	0.1436	0.1977	
200	0.0674	0.0602	0.0491	0.1005	0.1505	0.1963	
400	0.0690	0.0581	0.0491	0.1016	0.1445	0.19 3 0	
800	0.0680	0.0597	0.0483	0.1055	0.1556	0.2013	

TABLE XXI. - Molecular Conductivity of Ammonium Iodide in a Mixture of 75 percent Glycerol with Water at 25° , 35° , 45° .

v	/: 25 ⁰	350	450
1.0	5.48	8.24	11.61
1.3	5.39	8.11	11.53
2.0	5.24	8.00	11.50
4.0	5.18	7.99	11.47
10	5.26	8.16	11.75
50	5.56	8.64	12.56
100	5.71	8.89	12.94
200	5.81	9.05	13.19
400	5.76	8.99	13.18
800	6.06	9.44	13.74
1600	6.03	9.39	13.73

TABLE XXII. - <u>Temperature</u> <u>Coefficients</u>.

Per Cent.

Cond. Units.

		and the second		
v	25°-35°	35 ⁰ -45 ⁰	25°-35°	35 [°] -45 [°]
$ \begin{array}{c} 1.0\\ 1.3\\ 2.0\\ 4.0\\ 10\\ 50\\ 100\\ 200\\ 400\\ 800\\ 1600 \end{array} $	0.0504 0.0505 0.0527 0.0542 0.0551 0.0557 0.0557 0.0558 0.0561 0.0560 0.0557	0.0409 0.0422 0.0437 0.0435 0.0440 0.0454 0.0456 0.0457 0.0466 0.0456 0.0456 0.0456	0.276 0.272 0.276 0.281 0.290 0.318 0.318 0.324 0.323 0.329 0.339 0.336	$\begin{array}{c} 0.337\\ 0.342\\ 0.350\\ 0.348\\ 0.359\\ 0.392\\ 0.405\\ 0.414\\ 0.419\\ 0.430\\ 0.434\end{array}$

TABLE XXIII. - <u>Molecular Conductivity of Ammonium Iodide in</u> <u>a Mixture of 50 per cent Glycerol with Water</u> <u>at 25°, 35°, 45°</u>.

v	< 25 ⁰	350	Le. 450
1.0	22.38	29.40	37.24
1.3	22.19	29.36	37.25
2.0	22.12	29.51	37.55
10	23.15	31.27	40.34
50	24.69	33.4 0	43.16
100	25.52	34.54	44.83
200	25.49	34.66	45.18
400	25.68	35.20	45.30
800	26.29	35.87	46.18
1600	26.62	36.21	47.00

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TABLE XXIV. - Temperature Coefficients.

Per Cent.

Cond. Units.

v	250_350	35 ⁰ -45 ⁰	25 ⁰ -35 ⁰	35 [°] -45 [°]
1.0	$\begin{array}{c} 0.0314 \\ 0.0323 \\ 0.0334 \\ 0.0351 \\ 0.0353 \\ 0.0353 \\ 0.0353 \\ 0.0360 \\ 0.0371 \\ 0.0364 \\ 0.0364 \end{array}$	0.0267	0.702	C.784
1.3		0.0269	0.717	O.789
2.0		0.0272	0.739	O.804
10		0.0290	0.812	O.907
50		0.0292	0.871	O.976
100		0.0301	0.902	I.029
200		0.0303	0.917	I.052
400		0.0287	0.952	I.010
800		0.0287	0.958	I.031
800	0.0364	0.0287	0.958	1.031
1600	0.0360	0.0298	0.959	1.079

TABLE XXV. - Molecular Conductivity of Ammonium Iodide in <u>a Mixture of 25 per cent Glycerol with Water</u> <u>at 25°, 35°, 45°</u>.

V	1 25°	(; 35 ⁰	450
10	61.58	76.71	92.62
50	64.32	80.30	98.25
100	66.69	82.86	101.50
200	68.5 4	85.87	104.39
400	68.12	85.07	104.17
800	69.21	87.26	105.92
1600	69.68	88.47	106.85

TABLE XXVI. - Temperature Coefficients.

	Per	Cent.	Cond. Units.		
v	25°-35°	35 [°] -45 [°]	25 ⁰ -35 ⁰	350-450	
10 50 100 200 400 800 1600	0.0246 0.0248 0.0242 0.0256 0.0249 0.0261 0.0269	0.0207 0.0223 0.0225 0.0201 0.0224 0.0214 0.0208	1.513 1.598 1.617 1.733 1.695 1.805 1.879	1.591 1.795 1.864 1.852 1.910 1.866 1.838	

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TADLE A	AVII Molecular Conduc	LIVILY OI Ammonium	100100
	in Water at 25°,	$35^{\circ}, 45^{\circ}.$	
v	25 °	35°	450
1.3	100.7	114.1	130.4
2	102.5	125.3	147.5
4	105.3	125.8	151.3
10	121.3	148.6	172.6
50	135.2	160.5	186.3
100	136.3	161.3	190.8
200	139.0	168.5	197.7
400	143.1	171.2	202.9
800	151.1	182.0	215.1
1600	154.7	184.6	218.4

TABLE XXVII. - Molecular Conductivity of Ammonium Iodide

TABLE XXVIII. - Temperature Coefficients.

Per Cent.

Cond. Units.

v	25 [°] -35 [°]	35 [°] -45 [°]	25 ⁰ -35 ⁰	35 [°] -45 [°]
1.3	0.0133	0.0143	1.34	1.63
2	0.0222	0.0178	2.28	2.22
4	0.0195	0.0202	2.05	2.55
10	0.0225	0.0161	2.73	2.40
50	0.0187	0.0160	2.53	2.58
100	0.0184	0.0182	°2.50	2.95
200	0.0212	0.0173	2.95	2.92
400	0.0196	0.0185	2.81	3.17
800	0.0204	0.0176	3.09	3.21
1600	0.0193	0.0183	2.99	3.38

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TABLE XXIX. - Molecular Conductivity of Rubidium Bromide

in a Mixture of 75 per cent Glycerol with

<u>Water at 25° , 35° , 45° </u>.

v	Niv 250	M. 350	450
1.33 2 4 10	5.33 5.31 5.39 5.43 5.67	7.81 7.94 8.05 8.28 8.63	10.87 11.07 11.57 11.79 12.31
50 100 200 400 800 1600	6.15 6.27 6.35 6.41 6.52 6.52	9.31 9.67 9.79 9.87 10.03 10.07	13.46 13.86 14.11 14.28 14.45 14.51

TABLE XXX. - Temperature Coefficients.

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Ρ	ρ	r	(7	ρ	n	t		
ـ	◡	÷		•	$\overline{\mathbf{C}}$	11	υ.	٠	

Cond. Units.

	······································			
V	25°-35°	350-450	25°-35°	350_450
1	0.0465	0.0392	0.248	0.306
1.33	0.0495	0.0394	0.263	0.313
2	0.0494	0.0437	0.266	0.352
4	0.0525	0.0424	0.285	0.351
10	0.0522	0.0426	0.296	0.368
50	0.0514	0.0446	0.316	0.415
100	0.0542	0.0433	0.340	0.419
200	0.0542	0.0441	0.344	0.432
400	0.0540	0.0448	0.346	C.441
800	0.0538	0.0441	0.351	0.442
1600	0.0544	0.0441	0.355	0.444

TABLE XXXI. - Molecular Conductivity of Rubidium Bromide

in a Mixture of 50 per cent Glycerol with

Water at 25°, 35°, 45°.

۷	25 ⁰	6 35°	4, 450
1.	21.65	27.98	35.27
1.33	21.38	28.33	36.37
2	22.31	28.90	36.75
4	23.33	30.84	39.31
10	24.51	32.73	41.85
50	26.25	34.85	44.92
100	26.87	36.02	46.72
200	27.54	37.01	48.17
4 00	27.97	37.47	48.39
800	28.47	38.35	49.60
1600	28.39	38.33	49.48

TABLE XXXII.- Temperature Coefficients.

Per Cent.

Cond. Units.

v	25°-35°	350_450	25°-35°	350_450
1	0.0292	0.0261	0.633	0.729
1.33 2	0.0325 0.0295	0.0284 0.0280	0.695 0.659	0.80 4 0.785
4	0.0321	0.0281	0.751	0.847
10 50	0.0335 0.0328	0.0279 0.0289	0.822 0.860	0.912 1.007
100	0.0340	0.0297	0.915	1.070
200 400	0.0344 0.0340	0.0301 0.0292	0.9 47 0.950	1.116 1.092
800	0.0347	0.0293	0.988	1.125
1600	0.0350	0.0291	0.994	1.115

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TABLE XXXIII. - <u>Molecular Conductivity of Rubidium Bromide</u> in a <u>Mixture of 25 per cent Glycerol with</u> <u>Water at 25[°], 35[°], 45[°]</u>.

V	liv 250	2 [°] 1 [°] 35 [°]	450
2	51.79	65.77	79.87
4	54.23	67.23	81.80
10	62.88	76.85	93.67
50	69.27	84.84	103.77
100	69.44	86.22	105.46
200	71.39	89.09	108.43
4 00	73.40	91.15	111.22
800	74.16	92.10	111.81
1600	82.85	101.59	123.19

TABLE XXXIV. - Temperature Coefficients.

	Per C	ent.	Cond. Units.		
v	25°-35°	35°-45°	250_350	350-450	
2 4 10 50 100 200 400 800 1600	0.0270 0.0240 0.0222 0.0225 0.0239 0.0248 0.0242 0.0242 0.0242 0.0242 0.0226	0.0214 0.0217 0.0219 0.0223 0.0223 0.0217 0.0220 0.0214 0.0213	1.398 1.300 1.397 1.557 1.678 1.770 1.775 1.794 1.874	1.410 1.457 1.682 1.893 1.924 1.934 2.007 1.971 2.160	

TABLE XXXV	Molecular Conduc	tivity of Rubidium	n Bromide
	in Water at 25°,	$35^{\circ}, 45^{\circ}.$	
v	10, 25°		450

119.8

132.1

143.8

163.0

167.2

170.1

174.9

179.1

179.9

TABLE	XXXVI.	-	Temperature	Coefficients.

96.3

107.8

121.8

137.2 142.2 143.3

148.4

152.8

151.8

2

4

10

50

100

200

400

800

1600

Per Cent.

Cond. Units.

v	25 [°] -35 [°]	35 ⁰ -45	25 ⁰ -35 ⁰	350-450
2 4 10 50 100 200 400 800	0.0243 0.0226 0.0181 0.0188 0.0176 0.0187 0.0178 0.0172	0.0147 0.0160 0.0153 0.0162 0.0169 0.0175 0.0156 0.0163	2.35 2.43 2.20 2.58 2.50 2.68 2.65 2.63	1.76 2.12 2.20 2.63 2.82 2.98 2.98 2.73 2.92
1600	0.0185	0.0177	2.81	3.18

137.4

153.3

165.8

189.3

195.4

199.9

202.2

208.3

211.7

TABLE XXXVII. - Comparison of Temperature Coefficients of Ammonium Iodide from 25° to 35° in Mixtures of Glycerol and Water.

∇	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10 50 100 200 400 800 1600	0.1047 0.1061 0.1070 0.1082 0.1030 0.0923 0.0964	0.0551 0.0572 0.0557 0.0558 0.0561 0.0560 0.0557	0.0351 0.0353 0.0353 0.0360 0.0361 0.0364 0.0360	0.0246 0.0248 0.0242 0.0256 0.0256 0.0249 0.0261 0.0269	0.0225 0.0187 0.0184 0.0212 0.0196 0.0202 0.0193

TABLE XXXVIII. - <u>Comparison of Temperature Coefficients of</u> <u>Rubidium Bromide from 25[°] to 35[°] in Mixtures</u> <u>of Glycerol and Water</u>.

v	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10	0.1037	0.0522	0.0335	0.0222	0.0181
50	0.1071	0.0514	0.0328	0.0225	0.0188
100	0.1057	0.0542	0.0340	0.0239	0.0176
200	0.1036	0.0542	0.0344	0.0248	0.0187
400	0.1011	0.0540	0.0340	0.0242	0.0178
800	0.1020	0.0538	0.0347	0.0242	0.0172
1600	0.1198	0.0544	0.0350	0.0242	0.0185

TABLE XXXIX. - Viscosity and Fluidity of Ammonium lodide in <u>Glycerol at 25°, 35°, 45°</u>. Mol. conc. $\eta 25^{\circ} \eta 35^{\circ} \eta 45^{\circ} \varphi 25^{\circ} \varphi 35^{\circ} 45^{\circ}$ 0.4847 0.9335 1.071 0.2273 1.00 4.399 2.063 0.4506 1.75 4.769 2.219 1.139 0.2097 0.8782 1.205 0.4246 5.119 2.355 0.1953 0.8295 0.50 1.205 1.275 1.325 1.77

0.1819 0.3982

0.1734 0.3812 0.7545 0.1716 0.3776 0.7509

0.7841

TABLE XL	Temperature	Coefficients of Fluidity.
Mol. conc.	25°-35°	35° -4 5°
1.0 0.75 0.50 0.25 0.10 Soly.	0.113 0.115 0.117 0.119 0.120 0.120	0.093 0.095 0.095 0.096 0.098 0.099

2.511

 $2.623 \\ 2.648$

5.498

5.766

5.826

0.25

0.10

Solv.

TABLE XLI.	- <u>Viscos</u> i	ty and Fl	uidity of	Ammoniu	um Iodide	in
	Glycero	<u>l at 55°</u> ,	<u>650, 750</u>	•		
Mol. conc.	7 55°	17 65°	275°	\mathscr{O} 55 $^{\mathrm{O}}$	∉ 65 ⁰	750
1.00	0.5927	0.3623	0.2264	1.687	2.760	4.416
0.75	0.6215	0.3772	0.2344	1.609	2.651	4.266
0.50	0.6540	0.3850	0.2424	1.529	2.597	4.126

0.10 0.7060 0.4028 0.2577 1.416 2.482 3.880

Solv. 0.7100 0.4076 0.2558 1.408 2.453 3.909

1.469 2.523 3.975

0.25 0.6807 0.3963 0.2516

TABLE XLII.	- Temperature	Coefficients of Flu	uidity.
Mol. conc.	45 ⁰ -55 ⁰	55°-65°	65 ⁰ -75 ⁰
1.00	0.081	0.063	0.060
0.75	0.083	0.065	0.061
0.50	0.084	0.070	0.059
0.25	0.087	0.072	0.058
0.10	0.087	0.075	0.056
Solv.	0.087	0.074	0.059

TABLE XLIII Viscosity and Fluidity of Rubidium Chloride							
	in Glycerol at 25° , 35° , 45° .						
Mol. conc.	12 250	7 35°	1/ 45°	Ø 25 ⁰	> 35 ⁰	45 ⁰	
1.00	5.240	2.439	1.264	0.1908	0.4099	0.7910	
0.75	5.351	2.500	1.282	0.1869	0.4000	0.7801	
0.50	5.542	2.547	1.307	0.1804	0.3926	0.7651	
0.25	5.711	2.616	1.328	0.1751	0.3823	0.7531	
0.10	5.818	2.669	1.346	0.1719	0.37 41	0.7428	
Solv.	5.880	2.683	1.350	0.1701	0.3727	0.7407	

MADIW VITIE Viscogity and Pluidity of Rubidium Colorid

TABLE XLIV. - Temperature Coefficients of Fluidity.

Mol. conc.

1.00	0.115	0.095
0.75	0.114	0.095
0.50	0.118	0.095
0.25	0.118	0.097
0.10	0.118	0.098
Solv.	0.119	0.099

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TA	TABLE XLV Viscosity and Fluidity of Rubidium Chloride in						
		<u>Glycero</u>	<u>1 at 55°</u>	, <u>65⁰</u> , <u>7</u>	5°.		
Mo	l. conc.	7 55°	n 65°	750	arphi 550	¢ 65°	750
	1.00	0.6867	0.4177	0.2595	1.456	2.394	3.854
	0.75	0.6922	0.4195	0.2589	1.445	2.384	3.862
	0.50	0.7043	0.4341	0.2604	1.420	2.307	3.840
*	0.25	0.7130	. 4423	0.2608	1.403	2.263	3.834
	0.10	0.7224	0.4470	0.2606	1.384	2.237	3.831
	Solv.	0.7218	0.4505	0.26120	1.385	2.220	3.828

TABLE XLVI. - Temperature Coefficients of Fluidity.

Mol. cone.	45 [°] -55 [°]	55°-65°	65 ⁰ -75 ⁰
1.00	0.084	0.064	0.061
0.75	0.085	0.065	0.062
0.50	0.086	0.062	0.069
0.25	0.086	0.061	0.069
0.10	0.086	0.068	0.071
Solv.	0.087	0.060	0.072

TABLE XLVII	<u>Viscos</u>	sity and	Fluidity	y of Rubic	dium Brom	<u>ide in</u>
	Glycer	ol at 2	5 ⁰ , <u>35</u> ⁰ ,	<u>45</u> °.		
Mol. conc.	7 25°	Ŋ 35°	7 45°	φ 250	350	<i>↓</i> 450
1.00	4.965	2.307	1.199	0.2014	0.4335	0.8339
0.75	5.177	2.39 3	1.228	0.1931	0.4178	0.8146
* 0.50	5.388	2.472	1.274	0.1856	0.4044	0.7849
0.25	5.623	2.565	1.284	0.1778	0.3898	0.7785
0.10	5.858	2.650	1.338	0.1707	0.3773	0.7473
Solv.	5.885	2.664	1.358	0.1699	0.3754	0.7359

TABLE XLVIII. - <u>Temperature</u> <u>Coefficients</u>.

	25°_35°	35°-45°
1.00	0.115	0.092
0.75	0.116	0.095
0.50	0.118	0.094
0.25	0.114	ି . ୦୨୨
0.10	0.121	0.098
Solv.	0.121	0.096

* Calculated values from the N. sol.

TABLE XLIX.	- Viscos	ity and F	luidity o	f Rubidi	um Bromi	de in	
	<u>Glycerol at 55°, 65°-75°</u>						
Mol. conc.	N 550	.7 65°	75°	 ↓ 55[°] 	65 ⁰	- 75 ⁰	
1.00	0.6483	0.3967	0.2457	1.542	2.520	4.070	
0.75	0.6603	0.4041	0.2484	1.514	2.474	4.025	
0.50	0.6789	0.4108	0.2528	1.473	2.434	3.955	
0.25	0.6990	0.4146	0.2554	1.430	2.412	3.915	
0.10	0.7096	0.4226	0.2589	1.409	2.366	3.863	

Solv. 0.7121 0.4259 0.2604 1.404 2.348 3.840

TABLE	LX.	-	Temperature	<u>Coefficients</u> .
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	45 [°] -55 [°]	55°-65°	650-750
1.00	0.085	0.063	0.062
0.75	0.086	0.063	0.063
0.50	0.084	0.065	0.062
0.25	0.084	0.069	0.062
0.10	0.089	0.068	0.063
Solv.	0.091	0.067	0.068

TABLE LXI Viscosity and Fluidity of Rubidium Lodide in							
	<u>Glycerol at 25°, 35°, 45°</u> .						
Mol. conc.	n 250	r 350	h 450	L 25 ⁰	350	_ 450	
1.00	4.613	2.163	1.121	.2168	0.4623	0.8916	
0.75	4.912	2.292	1.181	0.2036	0.4362	0.8468	
0.50	5.159	2.365	1.209	0.1938	0.4228	0.8269	
0.25	5.566	2.554	1.294	0.1797	0.3915	0.7729	
0.10	5.769	2.628	1.328	0.1733	0.3804	0.7529	
Solv.	5.854	2.669	1.341	0.1708	0.3746	0.7457	

TABLE LXII	Temperature	Coefficients	of Fluidity.
Mol. conc.	28	5°-35°	35°-45°
1.00	0.	.113	0.093
0.75	0.	.114	0.096
0.50	0.	.118	0.096
0.25	0	.118	0.097
0.10	0	.119	C.098
Solv.	0.	.119	0.099

TABLE LXIII Viscosity and Fluidity of Rubidium Iodide in						
	Glyce	erol at 55	⁰ , <u>65⁰</u> , <u>7</u>	50.		
Mol. conc.	n 55°	17 65°	17 75°	<i>∅</i> 55 ⁰	φ 65°	4 ² 75 ⁰
1.00	0.6184	0.3763	0.2355	1.617	2.657	4.246
0.75	0.6436	0.3892	0.2420	1.554	2.569	4.132
0.50	0.6585	0.3981	0.2472	1.519	2.512	4.044
0.25	0.6955	0.4132	0.2548	1.422	2.420	3.924
0.10	0.7102	0.4236	0.2566	1.408	2.360	3.898
Solv.	0.7144	0.4243	0.2581	1.400	2.357	3.874

TABLE LXIV	E LXIV Temperature Coefficients of Fluidity.				
Mol. conc.	45°-55°	55 ⁰ -65 ⁰	65 ⁰ -75 ⁰		
1.00	0.081	0.064	0.060		
0.75	0.083	0.065	0.061		
0.50	0.084	0.065	0.061		
0.25	0.084	0.070	0.062		
0.10	0.087	0.068	0.065		
Solv.	0.088	0.068	0.064		

TABLE LXV.	- <u>Viscosi</u>	ity and H	Fluidity	of Rubidi	ium Nitrat	te in	
<u>Glycerol at 25°, 35°, 45°</u> .							
Mol. conc.	η 25°	n 35°	/ 45°	4° 25 ⁰	د [°] 35 ⁰	45 ⁰	
0.50	4.639	2.355	1.204	0.2156	0.4246	0.8307	
0.25	5.571	2.552	1.294	0.1795	0.3918	0.7727	
0.10	5.787	2.634	1.338	0.1728	0.3796	0.7473	
Solv.	5.854	2.669	1.341	0.1708	0.3746	0.7457	

TABLE LXVI	Temperature Coeffici	ents of Fluidity.
Mol. conc.	25 ⁰ -35 ⁰	35°-45°
0.50	0.097	0.096
0.25	0.118	0.098
0.10	0.120	0.097
Solv.	0.119	0.099

TABLE LXVII Viscosity and Fluidity of Rubidium Nitrate						
	<u>in</u> GJ	lycerol at	<u>55°, 65</u>	$\frac{75^{\circ}}{75^{\circ}}$.		
Mol. conc.	2 55°	? 65°	7 75°	Cî 55 0	£ 65 ⁰	750
0.50	0.6530	0.3982	0.2471	1.531	2.511	4.046
0.25	0.6955	0.4179	0.2561	1.438	2.393	3.904
0.10	0.7099	0.4237	0.2570	1.409	2.360	3.891
Solv.	0.7144	0.4243	0.2581	1.400	2.357	3.874

TABLE LXVIII.	- Temperature	Coefficients of Flui	ldity.
Mol. conc.	4 5°-55°	55°-65°	65 ⁰ -75 ⁰
0.50	0.084	0.064	0.061
0.25	0.086	0.066	0.063
0.10	0.088	0.068	0.064
Solv.	0.088	0.068	0.064

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TABLE LXIX.	- <u>Viscosi</u>	ty and Fl	uidity of	Ammoniu	um Iodide	in
	<u>75%</u> Gly	rcerol wit	h water a	t 25°, 3	<u>55°, 45°</u> .	
Mol. conc.	7 25°	₽ 35°	17 45°	(1 [°] 25 [°]	ψ 35°	41 450
1.00	0.2548	0.1580	0.1049	3.925	6.327	9.529
0.75	0.2703	0.1656	0.1094	3.700	6.039	9 .13 8
0.50	0.2873	0.1754	0.1143	3.481	5.700	8.749
0.25	0.3058	0.1842	0.1193	3.270	5.429	8.383
0.10	0.3097	0.1873	0.1204	3.229	5.338	8.302
Solv.	0.3174	0.1902	0.1220	3.151	5.259	8.197

TABLE LXX	Temperature	<u>Coefficients</u>	of Fluidity.
Mol. conc.		250-350	350-450
1.00		0.0612	0.0506
0.75		0.0632	0.0513
0.50		0.0637	0.0535
0.25		0.0660	0.0544
0.10		0.0653	0.0555
Solv.		0.0669	0.0559

TABLE LXXI.		ty and Flu cent Glyce				
Mol. conc.	1 25°	7, 3 50	17 4 5 ⁰	4 ²⁵⁰	35 ⁰	د ¹ 45°
1.00	0.05335	0.03838	0.02821	18.74	26.05	35.45
0.75	0.05534	0.03950	0.02885	18.07	25.32	34.66
0.50	0.05793	0.04089	0.02967	17.26	24.46	33.70
0.25	0.06029	0.04230	0.03182	16.59	23.64	31.43
0.10	0.06064	0.04260	0.03092	16.49	23.47	32 ;34
Solv.	0.06174	0.04299	0.03092	16.20	23.26	32.34

TABLE LXXII.	- Temperature Coeffi	cients of Fluidity.
Mol. conc.	25 [°] -35 [°]	35 ⁰ -45 ⁰
1.00	0.0390	0.0361
0.75	0.0401	0.0369
0.50	0.0417	0.0378
0.25	0.0425	0.0329
0.10	0.0423	0.0379
Solv.	0.0432	0.0390

TABLE LXXIII. - <u>Viscosity and Fluidity of Ammonium Iodide</u> in <u>25 per cent Glycerol with water at</u> <u>25⁰, 35⁰, 45⁰</u>.

Mol. conc.	25 ⁰	7 350	17 45 °	4 ⁷ 250	∉`35 °	∝ '45 0
1.00	0.01802	0.01406	0.01124	55.49	71.12	88.97
0.75	0.01843	0.01436	0.01147	54.26	69.64	87.18
0.50	0.01910	0.01464	0.01157	52.36	68.31	86.43
0.25	0.01973	0.01501	0.01180	50.68	66.62	84.75
0.10	0.01997	0.01510	0.01182	50.07	66.22	84.60
Solv.	0.02018	0.01525	0.01189	49.55	65.57	84.10

TABLE LXXIV	Temperature	<u>Coefficients</u>	of Fluidity.
Mol. conc.	259	⁰ -350	35°-45°
1.00	0.(0282	0.0251
0.75	0.0	0283	0.0252
0.50	0.0	0305	0.0265
0.25	0.0	0314	0.0272
0.10	0.0	0322	0.0278
Solv.	0.0	0333	0.0282

TABLE LXXV <u>Viscosity of Ammonium Iodide in Water at</u> 25° , 35° , 45° .						
Mol. conc.	12 25°	<i>7</i> 350	// 45 °	y 25 ⁰	350	45 ⁰
1.00	0.00838	0.00695	0.00584	119.3	143.9	178.2
0.75	0.00869	0.00701	0.00589	115.1	142.7	169.8
0.50	0.00871	0.00705	0.00595	114.7	141.7	168.0
0.25	0.00877	0.00712	0.00590	114.0	140.4	169.4
0.10	0.00889	0.00717	0.00597	112.4	139.4	167.5
Solv.	0.00891	0.00720	0.00597	112.2	138.9	167.5

TABLE LXXVI.	- Temperature Coefficients of	f Fluidity.
Mol. conc.	25 [°] -35 [°]	35 ⁰ -45 ⁰
1.00	0.0206	0.0170
0.75	0.0240	0.0190
0.50	0.0235	0.0185
0.25	0.0232	0.0206
0.10	0.0240	0.0217
Solv.	0.0238	0.0205

TABLE LXXVII. - <u>Viscosity and Fluidity of Rubidium Bromide</u> in 75 per cent Glycerol with Water.

Mol. conc.	7 25°	7 35°	2.45°	250	⊘ `35 °	450
1.00	0.2753	0.1702	0.1137	3.627	5.874	8.797
0.75	0.2844	0.1756	0.1152	3.516	5.694	8.683
0.50	0.2944	0.1795	0.1169	3.396	5.570	8.556
0.25	0.3036	0.1838	0.1168	3.293	5.441	8.558
0.10	0.3108	0.1877	0.1184	3.217	5.327	8.432
Solv.	0.3135	0.1880	0.1209	3.189	5.319	8.270

TABLE LXXVIII.	- <u>Temperature</u> <u>Coefficients</u>	of Fluidity.
Mol. conc.	25°-35°	35 ⁰ - 4 5 ⁰
1.00	0.0619	0.0496
0.75	0.0619	0.0525
0.50	0.0640	0.0536
0.25	0.0652	0.0573
0.10	0.0656	0.0583
Solv.	0.0668	0.0555

TABLE LXXIX. - <u>Viscosity and Fluidity of Rubidium Bromide</u> in 50 per cent Glycerol with Water.

Mol. conc	250	1/7 35 ⁰	7 45 [°]	o 25 ⁰	35 ⁰	450
1.00	0.05514	0.03958	0.02906	18.14	25.27	34.4]
0.75	0.05625	0.04035	0.02946	17.78	24.78	33.95
0.50	0.05791	0.04064	0.03014	17.27	24.61	33.18
0.25	0.05915	0.04194	0.03018	16.91	23.90	33.13
0.10	0.05986	0.04207	0.03029	16.71	23.77	33.01
Solv.	0.06021	0.04229	0.03035	16.61	23.65	32.95

TABLE LXXX.	- Temperature Coefficients	of Fluidity.
Mol. conc.	25 [°] -35 [°]	35 ⁰ -45 ⁰
1.00	0.0393	0.0362
0.75	0.0394	0.0370
0.50	0.0425	0.0348
0.25	0.0414	0.0386
0.10	C.0423	0.0389
Solv.	0.0424	0.0393

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TABLE LXXXI. - Viscosity and Fluidity of Rubidium Bromide in 25 per cent Glycerol with Water.

Mol. conc	· 7 25°	350	[,] 45 ⁰	25 ⁰	35 ⁰	450
0.50	0.01931	0.01492	0.01179	51.80	67.03	84.81
0.25	0.01970	0.01505	0.01186	50.76	66.44	84.30
0.10	0.01996	0.01518	0.01190	50.09	65.88	84.06
Solv.	0.02017	0.01523	0.01191	49.59	65.64	83.97

TABLE LXXXII.	- Temperature Coefficients	of Fluidity.
Mol. conc.	250-350	350-450
0.50	0.0294	0.0265
0.25	0.0309	0.0269
0.10	0.0315	0.0276
Solv.	0.0324	0.0279

TABLE LXXXIII. - <u>Viscosity and Fluidity of Rubidium Bromide</u> in <u>Water at 25[°]</u>, <u>35[°]</u>, <u>45[°]</u>.

Mol.conc.	17 25°	ig 350	450	250	35 ⁰	450
0.50	0.00872	0.00718	0.00608	114.7	139.4	164.3
0.25	0.00882	0.00720	0.00600	113.2	138.8	166.7
0.10	0.00880	0.00717	0.00596	113.6	139.4	167.7
Solv.	0.00891	0.00720	0.00597	112.2	138.9	167.5

TABLE LXXXIV.	- Temperature Coefficients	of Fluidity.
Mol. conc.	25°-35°	35 ⁰ -450
0.50	0.0215	0.0179
0.25	0.0226	0.0201
0.10	0.0227	0.0203
Solv.	0.0238	0.0205

TABLE L	XXXV Percent	age Increase in flu	aidity of Normal
	Solutio	ns in Glycerol at a	$25^{\circ}, 35^{\circ}, 45^{\circ}.$
	25 ⁰	35 ⁰	45 ⁰
NH ₄ 1	32.4	28.4	22.9
RbI	26.3	23.4	19.6
RbBr	18.5	15.4	11.9
RbC1	12.2	9.9	6.8

TABLE LXXXVI. - Comparison of Percentage Increase in Fluidity of Glycerol by Ammonium Iodide and Rubidium Iodide at 25°.

Mol. conc.	NH ₄ I	RbI
1.0	32.4	26.3
0.75	22.2	19.2
0.50	13.9	13.1
0.25	6.0	5.2
0.10	1.1	1.5

TABLE LXXXVII. - <u>Percentage Increase in Fluidity of Glycerol</u> <u>Water Mixtures at 25⁰</u>.

	Mol. conc.	Glycerol.	75%	50%	25%	Water.
$\mathbb{NH}_4^{\mathbf{I}}$	l	32.4	24.5	15.7	11.9	6.3
RbBr	l	18.5	11.2	9.2	(8.8)	(4.5)

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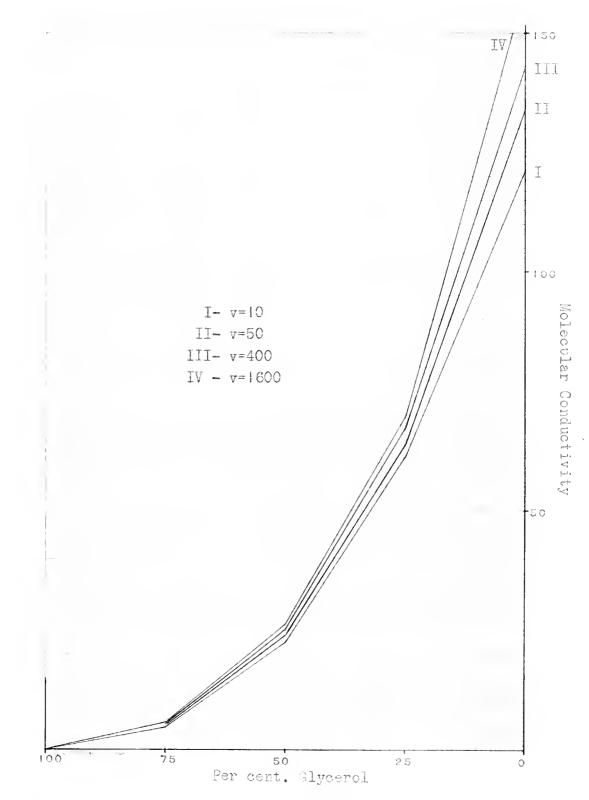


Fig.I--Conductivity of Annonius lodide in Glycercl-Water at 28°

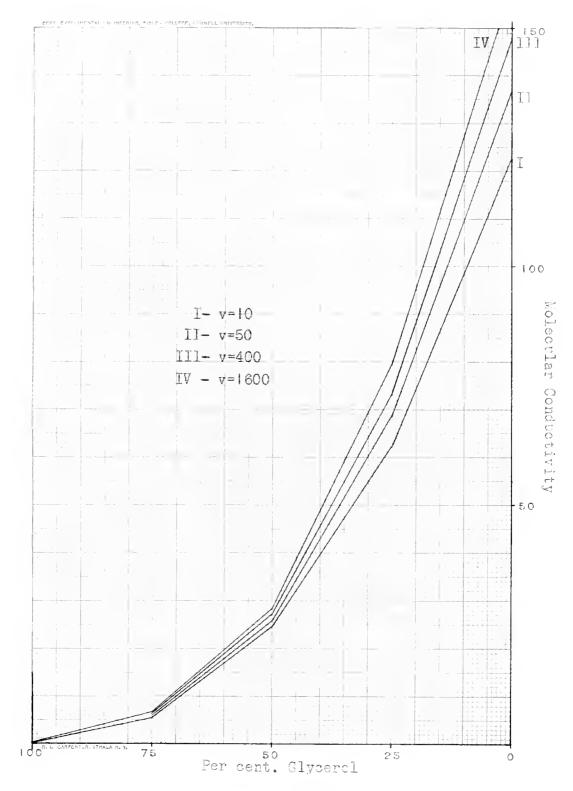
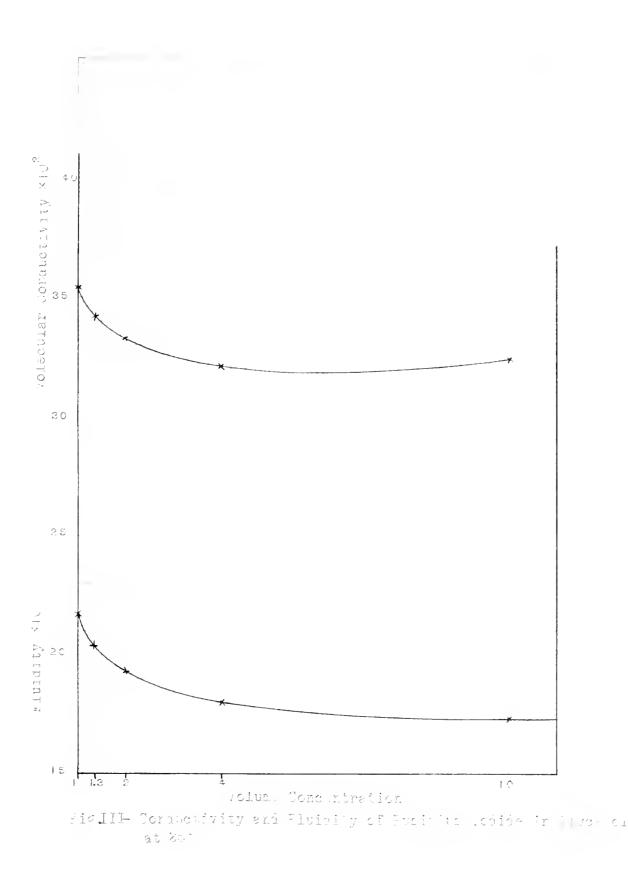
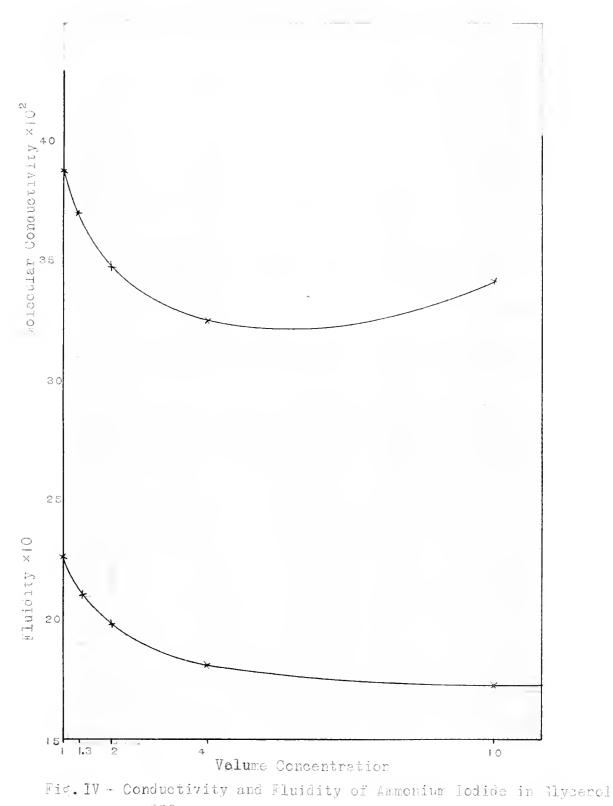


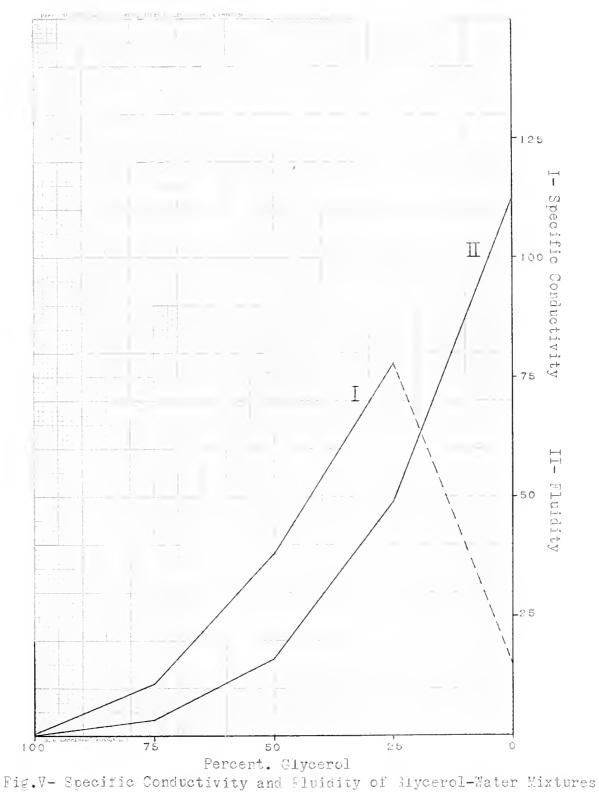
Fig.Jl- Conductivity of Rubidium Bromide in Glycerol-Water at 25°



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at 25°.



at 25°

DISCUSSION OF RESULTS -:-

The hypothesis of Dutoit and Aston, already referred to makes the dissociating power of a solvent a function of its own association. The degree of association of a solvent by the method of Ramsay and Shields has been shown to decrease with rise in temperature. Therefore, the increase in conductivity usually observed with rise in temperature can not be due to an increase in the number of ions present but must be caused by an increase in the velocity of those ions. As $Guy^{(1)}$ and others have already brought out, the change in the velocity of the ions with rise in temperature is to be ascribed to the change in the viscosity of the media surrounding the ions and in some instances, to the change in the mass of the ionic complexes formed by the ions and a certain number of molecules of the solvent.

Previous workers with glycerol as a solvent have already noted the enormous increase in conductivity of solutions in it with rise in temperature. While Guy has found some evidence for the existence of glycerolates, the writer believes the chief conditioning factor to be the change in the viscosity of the solvent. It is with the viscosity phenomena and chiefly with that of the lowering of the viscosity of glycerol by certain salts that this investigation has had to deal.

(1) Loc. cit.

Both conductivity and viscosity data have been obtained on the various salts studied and are presented in tabular form with accompanying tables of temperature coefficients.

Tables I to XX, inclusive, contain the molecular conductivities at ten degree intervals from 25° to 75° of ammonium iodide and of the several rubidium salts which I have studied in pure glycerol as a solvent. In agreement with the work of preceding investigators, viz., Schmidt and Guy, all the values for the are seen to be extremely low, much smaller than corresponding values in water. These values show a marked increase with rise in temperature and in the more dilute solutions $(N/10 t \circ N/1607)$ a regular increase with dilution. It is to be noted that in the more concentrated solutions, especially of the iodides, a decrease in conductivity takes place, the minimum lying as a rule close to the value for the N/10 solution. A discussion of this phenomenon will be taken up after a review of viscosity data.

The corresponding temperature coefficients of all the salts studied both in conductivity units and in percentages are of the same order of magnitude and show the same relative increase with increased dilution. This is to be expected since these salts are all binary electrolytes, and since all belong to that class whose cations possessing the largest atomic volumes have been shown to have little or no hydrating power in water. Such is not the case with ternary electrolytes in glycerol and especially with salts of calcium, strontium, barium and cobalt, the explanation of which has been fully given by Guy who bases

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his conclusions on the solvate theory. He points out that if there be solvation this should be more marked in the more dilute solutions where the amount of solvent per ion is greatest. Hence a change in temperature would produce the greatest effect where the solvation was greatest, viz., in the more dilute solutions and in solutions of those salts which have the greatest power of solvation.

The percent temperature coefficients are seen to be very large, being from ten to eleven percent between 25° and 35° . They decrease rapidly with rise in temperature, the value between 65° and 75° lying between four and a half and five percent. This may be partially accounted for by the enormous decrease in the viscosity of glycerol with rise in temperature. At 25° glycerol has a viscosity approximately 660 times that of water, while at 35° the value is 370 times that of water, but little more than half as great. At 75° the ratio falls to 70. In no other common solvent are the temperature coefficients of conductivity so great and the above ratios will show to some extent why this should be the case.

Tables XXI to XXXVI, inclusive, contain the molecular conductivities at 25° , 35° and 45° of ammonium iodide and rubidium bromide in mixtures of glycerol with water. Figures 1 and 2 express these results graphically. The solvents were prepared by diluting n. cc,of glycerol to one liter and denoting the resulting solvent as a mixture of n. percent.glycerol, with water.

It will be seen that the conductivity curves of such mixtures show a decided sagging. the conductivity values being always less than would be expected from the law of aver-The explanation of this has been given by Jones and ages. (1)and Jones and Murray⁽¹⁾ for mixtures of water with Lindsey the alcohols and has been extended to mixtures containing glycerol by Guy. A statement of the facts alone is necessary since reference has previously been made to this phenomenon. When two highly associated liquids are mixed, or, to take a specific instance, when glycerol is mixed with water, it has been shown that in such a case the properties of the mixture are not additive, each solvent tending to break down the association of the other; the combined dissociating effect of the two being less than would be expected had there been no such mutual diminution of the association. Guy has shown that in the case of glycerol mixtures with the alcohols, the diminution of the association takes place largely in the case of the glycerol.

In Tables XXXVII and XXXVIII a comparison is made of the temperature coefficients at $25^{\circ}-35^{\circ}$ of the two salts which we have studied in mixed solvents. These are seen to diminish the rapidly with addition of water, passing from 10 percent in pure glycerol to 2 percent in 25% glycerol.

The curve representing the specific conductivities of the various mixtures from glycerol to pure water is shown in Fig. 3. The values for 50% and 25% glycerol are larger than that for water. This is probably due to the presence of a few OH ions split off from the glycerol by action of the water.

NEGATIVE VISCOSITY -:-

A historical sketch of previous work in viscosity has already been given in the introductory part of this memoir. It is necessary therefore to take up here only the more important points.

Veazey's apparently satisfactory explanation of the phenomenon of negative viscosity has received ample corroboration by later workers. It will be remembered that he attributed the lowering of the viscosity of a solvent by a dissolved substance to the lessening in the skin friction between the molecules of the solvent and the molecules or ions of the solute in a given volume of the solution, because of the large atomic volumes of the cations, viz., potassium, rubidium and caseium, these three metals occupying the maxima on the atomic volume curve. Subsequent investigations have shown that certain ammonium salts in organic solvents, such as glycerol, are to be included in this category. Although we may not speak of the ammonium radicle NH_4 as having atomic volume, still it is well known that it possesses chemical properties closely allied to the alkali metals.

It is not surprising, therefore, to find negative viscoseffects ity, produced by ammonium salts, and from observations made by Guy on ammonium bromide, and from my own observations on ammonium iodide it is probable that the molecular complex NH₄ should occupy a place on the volume curve close to rubidium.

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In Tables XXXIX to LXVIII, inclusive, the viscosities and fluidities of ammonium iodide and of rubidium chloride, bromide, iodide and nitrate (1) in pure glycerol at 25° to 75° are given for a range of dilution from N to N/10. In every case the viscosity of the solution is less than that of the solvent. Even at 75° , rubidium chloride which increases the fluidity the least shows a positive fluidity coefficient of .3% for the N/10 solution.

A table of percent temperature coefficients of fluidity is given with each table of viscosities. These are seen to be almost equal to the temperature coefficients of conductivity but in every case are somewhat larger. This is to be accounted for by the decrease in association of the solvent with rise in temperature causing a decrease in the ionization of the solute and therefore a smaller conductive capacity. This would in part offset the increase in conductivity due to an increase in the velocity of the ions because of the decrease in viscosity of the solvent with rise in temperature.

The greatest viscosity lowering or increase in fluidity is to be observed in the case of the normal solution. This is obvious since the effect is proportional to the concentration. The dilution curve does not pass through a minimum but becomes asymtotic to that of the solvent at dilutions beyond the N/50. The percentage increase in fluidity becomes less also with rise in temperature, which may be accounted for by

(1) N/2 sol. saturated at 20° .

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the change in the molecular aggregates of the solvent and by the greater effect of temperature than of the dissolved salt on the viscosity of the solvent.

With the above facts in view, it is possible to explain the minima found at low temperatures in the conductivity curves for the concentrated solutions. These minima are more marked at 25° and in the case of those salts which give the greatest lowering of the viscosity of glycerol, viz., ammonium and rubidium iodides. In the concentrated solution (N - N/4) the ionization is nearly constant, while the negative viscosity effect decreases with increased dilution.

Reference to Fig. 3 will show that the conductivity and fluidity curves at 25° for rubidium iodide are practically parallel up to and through the N/10 solution. Beyond that dilution the increased ionization causes a rise in the conductivity curve while the fluidity curve becomes the asymptote of the solvent. Here we have conductivity varying directly as the fluidity or inversely as the viscosity. It is of interest to observe that a salt can lower the viscosity of a solvent to such an extent as to increase its own conductivity in that solvent. Fig. 4 shows similar results with ammonium iodide.

Table LXXXV shows the relative percentage increase in fluidity produced by normal solutions of the various rubidium salts and of ammonium iodide at $25^{\circ}-45^{\circ}$. It is evident that of the halogen salts of rubidium the iodide produces the greatest change in fluidity, followed by the bromide, then the chloride. This may be explained by the fact that when the cation,

here rubidium, to which the increase in fluidity is mainly due, remains the same, the negative viscosity effect is a function of the molecular volumes of the salt in question.

If we divide the molecular weights of the three halogen salts by their densities referred to water as a unit, we obtain the following values:

EbI, $\frac{212.37}{3.02} = 7.02$; RbBr $\frac{165.37}{2.78} = 5.95$; RbCl, $\frac{120.91}{2.20} = 5.496$. Reference to the table will show that the experimental data is in accord with this rubidium iodide at 25° producing a percent increase in fluidity of 26.3, rubidium bromide 18.5 and rubidium chloride 12.2. It was impossible to prepare a normal solution of rubidium nitrate in glycerol at the normal temperature 20°. The N/2 solution was nearly saturated at that temperature and shows somewhat greater negative viscosity coefficients than would be expected.

The N/4 solution, however, gives values between that of rubidium bromide and iodide which is to be expected from its molecular volume. No adequate explanation can be offered for the apparently abnormal negative viscosity coefficients of ammonium iodide in glycerol.

In Table LXXXVI is given the percentage increase in fluidity at 25° produced by the two salts showing the most marked negative viscosity effect, viz., rubidium iodide and ammonium iodide over the range of dilution studied. That the increase in fluidity is not exactly proportional to the concentration may be due to the slight increase in ionization in the more dilute solution the effect of the anions tending to offset

that of the cation.

Tables LXIX to LXXXIV, inclusive, show the viscosities and fluidities of rubidium bromide and ammonium iodide in glycerol-water mixtures at 25° , $35^{\circ}-45^{\circ}$. The addition of water to glycerol causes an enormous increase in fluidity. The curve representing the fluidity changes with decreasing percentages of glycerol shown in Fig. 5 is strikingly similar to the conductivity curves in those mixtures, (Figs.1 & 2).

The salts studied show negative viscosity in the glycerol water mixtures and in pure water at low temperatures. In water at 45° , rubidium bromide shows a tendency to pass over to positive viscosity altho the transition is not very marked.

The last Table (LXXXVII) gives a comparison of the percentage increase in fluidity produced by normal solution of the two salts in glycerol-water mixtures at 25°. The values do not follow the law of averages in such mixtures but are lower. This is in all probability due to the increased ionization in the mixed solvents, and also to the breaking down of the molecular complexes of the solvent which would in both cases give ultimate particles with greater frictional surfaces.

SUMMARY

The following points have either been confirmed or brought out in this dissertation:

<u>1.</u> Conductivity values in glycerol are extremely small but show regular increase with rise in temperature and except in special cases, with dilution.

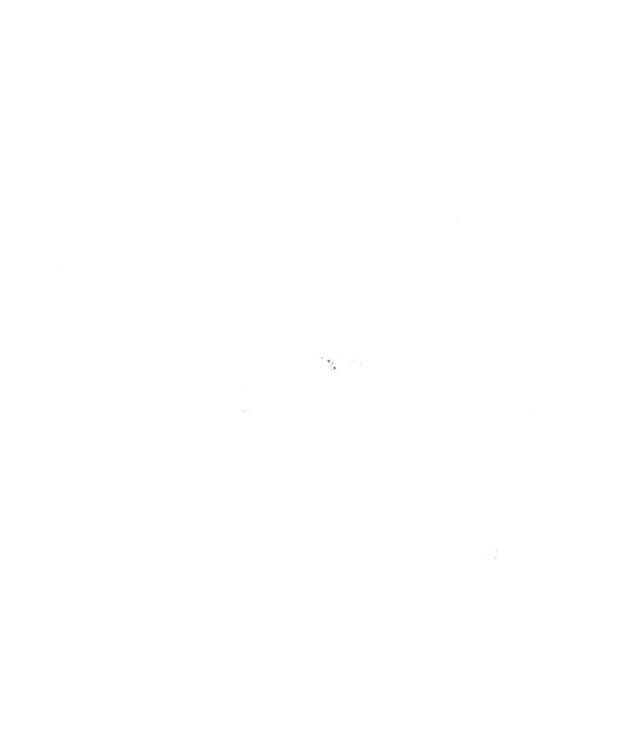
2. In the case of salts producing a marked lowering of the viscosity of the solvent, a minimum in the conductivity curve of the concentrated solutions has been noted, the conductivity varying directly with the fluidity.

3. Conductivities in glycerol-water mixtures do not follow the law of averages, but are always lower.

<u>4.</u> Rubidium salts produce a phenomenal lowering of the viscosity of glycerol, much greater than that of corres-

5. Ammonium salts seem more closely allied to rubidium than to potassium in their effect on the viscosity of a solvent like glycerol.

<u>6.</u> The percentage increase in fluidity of the solvent produced by the dissolved salt becomes less with rise in temperature and with dilution.



7. Rubidium salts in pure glycerol show no tendency to produce positive viscosity even at 75° .

8. Curves representing fluidity and conductivity in mixtures of glycerol and water show marked similarity over the range of temperature studied.

Paul Bell Davis, the author of this dissertation, was born in West Liberty, Logan County, Ohio, August 15th, 1889. At an early age, he removed with his parents to Salem, Virginia, and in the public schools of this town he received his preliminary training. After studying one year at the Salem High School, he entered the freshman class of Roanoke College in the fall of 1904. From this institution he received the degree of Bachelor of Arts in 1908.

During the year 1908-09, he was assistant in chemistry and was awarded the degree of Master of Arts in June 1909. In the fall of 1909, he entered the Johns Hopkins University as a graduate student in chemistry. His subordinate subjects were physical chemistry and mineralogy.

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