sulfide reductions.   It is believed that they are polythionic acids and it has been noted that (1) they are quite stable upon boiling with sulfuric acid in concentrations as high as 33% by volume; (2) they are volatile upon prolonged boiling; (3) the volatilized compounds do not react with iodine solution; and (4) their dilute solutions give with silver nitrate solution a yellowish-brown coloration.

V. Summary.

1. The determination of iron or of vanadium by reduction with hydrogen sulfide followed by titration with permanganate or dichromate ordinarily gives high values.

2. These high values are not due to the presence of sulfur and persist in spite of the complete expulsion of hydrogen sulfide and the avoidance of organic matter extracted from filter paper.   They may be ascribed to polythionic acids which are not destroyed by boiling in moderately conc. sulfuric acid solution and which are volatilized slowly from dilute and more rapidly from concentrated solutions.

3. Reasonably accurate determinations may be made by restricting the original solution to 100 cc. and proceeding by the described modified method.

4. For accurate determinations of iron and vanadium in solutions containing platinum (as in rock analysis) a preliminary separation of the hydrogen sulfide group, followed by expulsion of the gas, complete oxidation with permanganate and reduction with sulfur dioxide is recommended.

The authors desire to express to Dr. W. F. Hillebrand their sincere appreciation of his aid and counsel.

WASHINGTON, D. C.

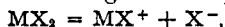## THE CONDUCTANCE OF SOLUTIONS OF TERNARY ELECTROLYTES IN PROPYL ALCOHOL.

BY CHARLES A. KRAUS AND JOHN EGBERT BISHOP.

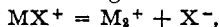### I. Introduction.

Our knowledge of the ionization process of ternary electrolytes in non-aqueous solvents is very limited and even in the case of aqueous solutions the nature of the ionization process for these substances is uncertain.   If intermediate ions are formed according to the equation
$$MX_2 = MX^+ + X^-,$$
which, in turn, break down according to the equation
$$MX^+ = M_2^+ + X^-,$$
then it is not possible to determine the equilibrium in the solution by means

of conductance measurements alone. In view of the fact that the laws governing solutions of strong electrolytes are not known, other properties of these solutions cannot be employed to supply the additional relation necessary to obtain a solution of the problem. In the case of weak acids and bases it has been shown that intermediate ions are formed. Noyes and Eastman[1] have established that a similar process takes place in solutions of sulfuric acid. In the case of salts, however, no definite evidence exists to show that intermediate ions are formed, although Harkins,[2] from the effect of various electrolytes upon the solubility of difficultly soluble salts of higher type, has reached the conclusion that intermediate ions do, in fact, exist.

Schlamp[3] measured the conductances of solutions of sodium iodide, lithium chloride and calcium chloride in propyl alcohol. Völlmer[4] drew from Schlamp's results the conclusion that calcium chloride behaves like a binary electrolyte in propyl alcohol solution, its conductance curve lying intermediate between those for lithium chloride and sodium iodide and being approximately parallel to them. It seemed worth while to measure the ionization of a number of ternary electrolytes in propyl alcohol in order to determine whether Schlamp's results and Völlmer's conclusions therefrom could be substantiated. Incidentally, it may be stated that, in fact, Schlamp's values for the conductance of calcium chloride solutions lie below those for lithium chloride and sodium iodide and not between them.

II. Apparatus and Materials.

The conductance cell employed consisted of a cylindrical tube about 40 cm. long, having a capacity of approximately 200 cc. It was provided with platinized electrodes at the bottom and with a neck and a ground-glass stopper at the top. This neck was bent at an angle of 60° with the axis of the cell in order to facilitate the process of mixing the solutions.

The cell constant was determined by means of 0.02 N and 0.01 N solutions of potassium chloride, whose specific conductance values at these concentrations were assumed to be 0.002397 and 0.001225 respectively. The constant of the cell was determined to be 0.2049 at 18.00°.

Propyl alcohol was prepared by repeated fractionation and was finally dehydrated by means of metallic sodium. Immediately before introducing into the cell, a small amount of sodium was added to the alcohol. It was then distilled directly into the conductance cell, the intermediate fraction only being used. The specific conductance of the pure solvent varied between 1.3 and 1.7 $\times 10^{-7}$. The value of the specific conductance of the solvent was in each case subtracted from that of the solution, the differ-

[1] Noyes and Eastman, "Electrical Conductivity of Aqueous Solutions," *Carnegie Inst. Pub.*, No. **63**, p. 239 (1907).

[2] Harkins, THIS JOURNAL, **33**, 1836 (1911).

[3] Schlamp, *Z. physik. Chem.*, **14**, 272 (1894).

[4] Völlmer, *Ann. Physik.*, **22**, 328 (1894).

ence being assumed to give the true value for the specific conductance of the electrolyte in solution.

The salts employed were anhydrous calcium nitrate and the hexahydrate of magnesium nitrate. The calcium nitrate was imported c. p. material and was further purified by two crystallizations from doubly distilled water and finally from conductivity water. Contrary to the statement made in Abegg's "Handbuch der Anorganischen Chemie," it was not found possible to dehydrate the crystallized salt at 160° in air. At the end of 3 days, so much water of crystallization remained that the entire mass was still completely liquid. The salt was then placed in a desiccator over phosphorus pentoxide which was then evacuated to a pressure as low as 0.001 mm. At the end of 5 days an appreciable amount of water still remained in the salt. It was then placed in one arm of an H-tube, the other arm of which was filled with phosphorus pentoxide. A plug of glass wool was placed between the two arms to prevent contamination of the salt. The tube was exhausted to a pressure below 0.001 mm. and sealed off. The limb containing the salt was then heated for 2.5 days in a water-bath at 100°; that containing the phosphorus pentoxide remaining at room temperature. At the end of that time no trace of water could be found.

The magnesium nitrate was an imported grade "For Analysis" and no further purification was attempted. It was at first intended to dehydrate this salt also, but the attempt was abandoned since, after treating for 4 days at 100° with phosphorus pentoxide in a high vacuum, a considerable amount of water was still left in the salt. As the crystallized salt is quite hygroscopic, the excess of moisture was removed by placing it in a tube and passing over it a current of air which had previously been passed through 3 ordinary potash bulbs filled with 40 % sulfuric acid, and thereafter filtered. Although the vapor pressure of sulfuric acid at this concentration is considerably above that given for $Mg(NO_3)_2.6H_2O$ at 20°, it was considered advizable to make a determination of the actual magnesium content of the salt. It was found that the salt contained 1.01 % of magnesium in excess of that corresponding to the above formula. This correction has been applied to the calculations.

Anhydrous barium nitrate was also prepared but could not be employed, as it was found to be only slightly soluble in the anhydrous alcohol. Strontium nitrate and strontium and barium chlorides were likewise found to be only slightly soluble, the last named salt being somewhat more soluble than the others.

The alcohol content of the cell was obtained by weighing. Because of the small amount of salt required for the more dilute solutions, these were made up by introducing into the cell a weighed quantity of a more concentrated solution. This solution was weighed in a small pipet, somewhat similar to an Ostwald pycnometer. The outlet tube was protected by means of a cap covering the end of the capillary and the other tube by means of a stopcock. This method of making up the solutions was employed in all cases, except that of calcium nitrate, where the last three concentrations were made by weighing the salt directly. Since the concentration never exceeded 0.1 normal, it was assumed that the density of the solutions is equal to that of the pure solvent, whose density is 0.8043 at 18°,

III. Experimental Results.

The results are given in the following table, in which the weight W of the concentrated solution added is given in the first column, the concentration

of the salt in millimols per liter is given in the second column, the molecular conductance Λ, corrected for the specific conductance of the solvent, in the third column, and the logarithm of the dilution V in the last column. At the head of the table the initial weight of the solvent is given under W_0, the specific conductance of the pure solvent under l_s, and the concentration of the added solution under C_s.

TABLE I.—CONDUCTANCE OF ANYHDROUS CALCIUM NITRATE IN ANHYDROUS PROPYL ALCOHOL AT 18.00°.

$W_0 = 141.075.$ $l_s = 1.7 \times 10^{-7}.$ $C_s = 0.008922.$

$W.$	$C \times 10^3.$	$\Lambda.$	Log $V.$
1.1780	0.363	5.140	3.4413
2.6023	0.792	3.834	3.1013
5.4169	1.617	2.894	2.7913
11.597	3.326	2.184	2.4781
22.006	5.908	1.798	2.2286
28.004	7.247	1.688	2.1398
0.4943	14.320	1.258	1.8441
0.8645	24.930	0.976	1.6033
1.4724	43.290	0.722	1.3636

To the most concentrated solutions was added 0.5795 g. of water. The concentration of the resulting solution was 43.27×10^{-3} mols per liter and its molecular conductance 2.036. On the further addition of 0.5023 g. of water to the same solution, the molecular conductance was raised to 2.991 at a concentration of 43.25×10^{-3} mols per liter.

The conductance values for magnesium hexahydrate in anhydrous propyl alcohol are given in Table II.

TABLE II.—CONDUCTANCE OF MAGNESIUM NITRATE HEXAHYDRATE IN ANHYDROUS PROPYL ALCOHOL AT 18.00°.

$W_0 = 93.005.$ $l_s = 1.53 \times 10^{-7}$ $C_s = 0.055941.$

$W.$	$C \times 10^6.$	$\Lambda.$	Log $V.$
0.2128	394	12.422	3.4045
0.4672	865	10.730	3.0630
1.0579	1942	8.932	2.7118
1.9588	3483	7.774	2.4581
3.5808	6406	6.408	2.1934
6.2129	9804	6.026	2.0086
12.757	1989	4.674	1.7014
25.324	3612	3.866	1.4423

In Table III are given the conductance values for magnesium nitrate hexahydrate in a mixture of propyl alcohol and water, containing 95.77 g. of propyl alcohol and 0.632 g. of water.

TABLE III.—CONDUCTANCE OF MAGNESIUM NITRATE HEXAHYDRATE IN A MIXTURE OF PROPYL ALCOHOL AND WATER.

$W_0 = \begin{cases} 95.77 \text{ g. } C_3H_8OH \\ 0.632 \text{ g. } H_2O. \end{cases}$ $l_s = 3.45 \times 10^{-7}$. $C_s = 0.08822$.

| W.	$C \times 10^6$.	Λ.	Log V.
0.1044	298	17.774	3.5258
0.6879	1950	9.062	2.7100
1.3343	3758	7.326	2.4260
2.3173	6339	6.188	2.1980
4.2986	11670	5.096	1.9329
7.376	19460	4.400	1.7009
12.019	30410	3.921	1.5170
21.210	49560	3.554	1.3049

IV. Discussion of Results.

The results are shown graphically in the accompanying figure, values of log V being plotted as abscissas and those of Λ, the molecular conductance, as ordinates. The nature of the electrolyte and the solvent is in each case shown on the figure. In the same figure are shown the conductance curves for sodium iodide, lithium chloride, and calcium chloride, obtained by Schlamp. Since calcium chloride, calcium nitrate, and magnesium nitrate are ternary salts, their molecular conductance, if ionization is anywhere near complete, should be approximately twice that of a binary electrolyte; while, if they ionized according to Equation I, their molecular conductance should be very nearly the same as that of binary electrolytes, the concentration, of course, being expressed in mols per liter.

It is evident from an examination of the curves that Völlmer's conclusion that calcium chloride ionizes according to a binary process is not justified. Schlamp's conductance curve for calcium chloride lies much below that for both lithium chloride and sodium iodide. Moreover, the curve for calcium chloride does not run parallel to that of the curves of the binary salts.

Another uncertainty in Schlamp's results lies in the fact that he has not specified the condition of his calcium chloride. This salt crystallizes as a hexahydrate and is dehydrated with great difficulty. Since he makes no mention of any facts in this connection, it is probable that he employed the hydrated salt. It is also probable that Schlamp's alcohol was not completely free from water, since he dehydrated it only with fused potassium carbonate. The presence of small amounts of water has a great influence upon the conductance curve of electrolytes which exhibit a marked tendency to form compounds containing water of crystallization.

Schlamp's curve for calcium chloride resembles that for the hydrated magnesium nitrate in anhydrous propyl alcohol. The conductance values for the hydrated salts in anhydrous propyl alcohol are relatively low at the

higher concentration and increase markedly at lower concentrations. There is no indication that these curves are approaching a limiting value as

Conductance of salts in propyl alcohol.
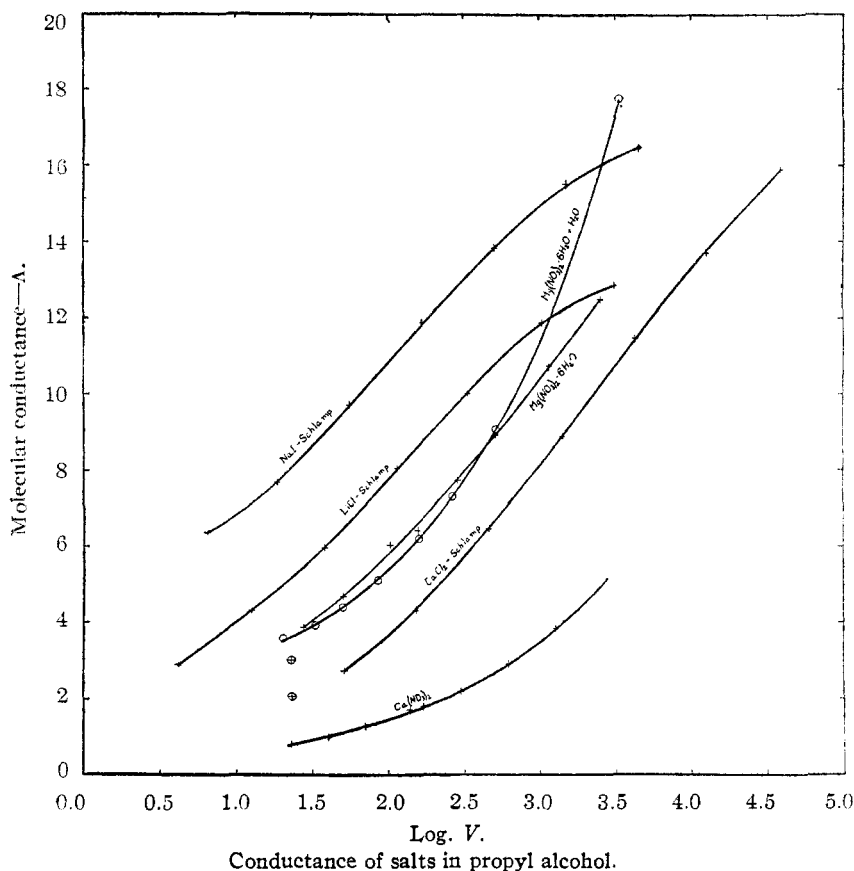
the concentration decreases, and it must therefore be assumed that ions of the type M^{++} are present.

No previous data are available on the influence of small additions of water upon the conductance of ternary electrolytes in non-aqueous solutions. In general, the conductance of ternary electrolytes in anhydrous solvents is relatively low. That the ionization is generally increased by the addition of water may be concluded from the work of Jones and his co-workers, who have measured the conductance of a considerable number of mixtures containing 25% of water. It is evident that the initial additions of water cause a large increase in the conductance of the solutions. The addition of 3.62% of water raises the molecular conductance of calcium nitrate from 0.772 to 2.036, or 2.64 times; while the addition of 6.75% raises it to 2.991, or 3.88 times the value in the anhydrous solvent. These

points are represented in the figure by $\oplus$ at the concentration log $V = 1.36$. A comparison of the conductance curves for magnesium nitrate hexahydrate in dry alcohol and in the presence of approximately 0.7% of water likewise clearly shows the influence of water upon the conductance of the solutions. The two curves intersect at two points. At low concentrations the additions of water cause a marked increase in the conductance of the solution, while at intermediate concentrations the addition of water causes a slight decrease in the conductance of the solution. It is to be presumed that at considerably higher concentrations the addition of water would cause a relatively large increase in the conductance of the solution. It is probable that the curve for anhydrous magnesium nitrate does not differ measurably from that for calcium nitrate. The diminution in the conductance due to the addition of water at intermediate concentrations of salt is probably due to the fact that on addition of larger amounts of water the ionic complexes formed have a relatively lower speed than those which contain less water. Somewhat similar results are obtained on the addition of water to solutions of acids.[5] When small amounts of water are added to solutions of strong acids in alcohol, the equivalent conductance of the acid is greatly reduced. This reduction appears to be due to the formation of a complex hydrogen ion whose speed is relatively low. It is interesting to note that on the addition of water to weak acids the conductance is increased and this increase is in general the greater the weaker the acid. This increase is apparently due to an increase in the ionization of the dissolved electrolyte, due to the addition of water. Lithium chloride in ethyl alcohol also shows a slight increase on addition of water. This influence of water upon the conductance of solutions of electrolytes which show a marked tendency to form complexes with water, is readily accounted for on the assumption that the ionization of the complex formed is greater than that of the non-hydrated electrolyte. This is in excellent agreement with Werner's theory of the constitution of salts.

V. Summary of Results.

1. The conductance of an anhydrous ternary salt in anhydrous propyl alcohol has been measured.

2. The effect of the addition of varying amounts of water to solutions of anhydrous ternary electrolytes in anhydrous propyl alcohol has been studied.

3. A comparison of the results of the present investigation with those of Schlamp indicates that he employed hydrated calcium chloride.

[5] Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1915).

4. A critical examination of the results obtained by Schlamp lends no support to the view that ternary salts in this solvent ionize according to a binary process.

WORCESTER, MASS.

[CONTRIBUTION FROM THE BUREAU OF SOILS AND THE FIXED NITROGEN RESEARCH LABORATORY.]

VAPOR PRESSURE OF LITHIUM NITRATE: AMMONIA SYSTEM.[1]

BY R. O. E. DAVIS, L. B. OLMSTEAD AND F. O. LUNDSTRUM.

In recent work on the absorption of ammonia from a mixture of hydrogen and nitrogen gases used in ammonia synthesis the desirability of employing as absorbent some substance other than water became evident.   A number of good absorbents for ammonia are known, but each has its disadvantages for our purpose.   Liquid absorbents seem more desirable than solid but only two other than water which meet most of the requirements have been mentioned in the literature.   The desirable qualities in an absorbing liquid are that its water vapor pressure be low over a considerable range in temperature and that the vapor pressure of ammonia vary considerably over a short range in temperature.   The liquid should be non-corrosive to ordinary metals so that it can be used as a circulating medium and should not cause any obstruction in the pipes, valves, or other parts of the system.

Solid ammonium nitrate treated with anhydrous ammonia liquefies, giving a liquid rich in ammonia and remaining liquid over considerable range in temperature.   This is the well known Divers Solution[2] and has been studied by Kuriloff.[3]   Similarly, ammonium thiocyanate forms a liquid with ammonia as first noted by Bradley and Alexander[4] and this has been studied by Foote and Hunter,[5] who have shown some of the desirable properties of this liquid for the purpose we have in mind; namely, the removal of ammonia from a mixture of gases and its subsequent recovery free from these gases.   However, a serious draw-back to the use of these liquids is that they attack metals rapidly.

In searching for a suitable liquid absorbent we have investigated substances listed by Franklin and Kraus,[6] as very easily soluble, easily soluble, and miscible in liquid ammonia.   A number of these were eliminated as undesirable for our purpose merely by inspection, but quite a number

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[1] Published by permission of the Chief of Ordnance, U. S. Army.
[2] *Chem. News*, **27**, 37.
[3] Kuriloff, *Z. physik. Chem.*, **25**, 107 (1898).
[4] Alexander, THIS JOURNAL, **34**, 15 (1914).
[5] Foote and Hunter, *ibid.*, **42**, 69 (1920).
[6] Franklin and Kraus, *Am. Chem. J.*, **20**, 820.