were used in this series, and the silver came from various sources, these variations being without effect on the result.

(11) If the atomic weight of silver is assumed to be 107.920, sodium is found from the above results to have an atomic weight of 23.006 and chlorine an atomic weight of 35.470.

(12) Many other atomic weights are affected, in their second decimal places, by these changes. In particular, certain slight anomalies previously noticed in Harvard work are explained by them, and the atomic weight of nitrogen computed from ammonia is brought nearer to the value required by Avogadro's rule. Other anomalies appear in other places, however, and it is clear that many new atomic-weight investigations must be instituted to explain them, with due attention to hitherto unheeded dangers, especially of occlusion.

CALCIUM SULPHATE IN AMMONIUM SULPHATE SOLUTION[1].

BY EUGENE C. SULLIVAN.

ARRHENIUS[2] rejects the idea of constant concentration of the non-dissociated portion of a salt in its saturated solution on the following grounds:

In a saturated water solution of thallous chloride (TlCl) the non-dissociated salt, calculated from the electric conductivity, is 0.00179 normal, while in the presence of 0.8 normal potassium chloride the total solubility of thallous chloride is only 0.00170 normal,[3] i. e., less than non-dissociated thallous chloride alone in pure water solution; of this 0.00170 perhaps 40 per cent. is dissociated, leaving the non-dissociated portion apparently in decidedly lower concentration than in the water solution. There are other similar cases.

Further, Arrhenius demonstrates that the isohydric principle applied to the calculation of conductivity of mixtures gives satisfactory results: Solutions having the same ion in equal concentration afford a mixture whose conductivity is a mean of the individual conductivities; that is, the dissociation in the case of iso-

hydric solutions is not affected by mixing. This is extended to any mixture of electrolytes having a common ion by imagining the mixture formed by bringing together isohydric solutions of such electrolytes. MacGregor[1] has formulated a graphic method of thus getting at the conductivity of mixtures, and the results agree excellently with those obtained by actual measurement. The point being thus established that the composition of the mixture, so far as it may be judged at all by the conductivity, is ascertainable by application of the isohydric method, Arrhenius calculates by this means the relative amounts of dissociated and nondissociated silver salt present in the case of sodium salts of certain organic acids saturated with the corresponding silver salts.[2] The solubilities of the silver salts in the solutions were determined by experiment, but no attempt was made to measure conductivity. The concentration of the non-dissociated silver salt in the saturated solution as thus calculated is not constant.

The measurements presented in the following paper, made originally for a somewhat different purpose, are found to show that the isohydric principle applied to ammonium sulphate solutions saturated with calcium sulphate gives results for the conductivity of the mixtures agreeing with those actually observed, and varying somewhat from those which might be expected if the concentration of non-dissociated calcium sulphate were the same throughout all the solutions.

The calcium sulphate used was in the form of perfectly clear transparent plates of gypsum, $CaSO_4.2H_2O$ (selenite). The only impurity detected was a faint trace of chloride. The ammonium sulphate, purified by repeated crystallization, contained a slight non-volatile residue (1.2 mg. in 10 grams) for which the corresponding correction was applied to the weight of calcium sulphate found.

The gypsum was coarsely broken, washed several times by decantation with the solvent, and slowly revolved (three revolutions per minute) in a thermostat at 25° C. The flasks used were of Jena glass, steamed, closed with rubber stoppers and sealed with paraffin. The solution after saturation was, without removal from the thermostat, filtered upward by suction through a very small paper filter into a second flask, also in the thermostat. For analysis a weighed quantity of the solution was evaporated

² *Trans. Nova Scotian Institute of Science,* **9**, 101 (1895).
¹ *Ztschr. phys. Chem.,* **31**, 224 (1899).

in platinum, the ammonium sulphate very slowly and carefully driven off by heat, the dish containing calcium sulphate heated to redness and weighed.[1] Known quantities of gypsum treated with sulphuric acid, which was then expelled by heat, gave results agreeing closely with those calculated. They ran pretty uniformly 0.1 per cent., rarely 0.2 per cent. higher than calculated. Known quantities of gypsum, mixed with ammonium sulphate and recovered in the same manner as in the case of the saturated solutions analyzed, gave somewhat greater variations, due to mechanical loss on driving off the ammonium salt, and also to retention of the latter even at high temperatures. The mean of duplicates worked in this way was usually, however, but 0.1 to 0.2 per cent. higher than the expected result.

For gypsum dissolving in water alone equilibrium was reached from either direction. Supersaturation was obtained by revolving one and a half hours at 35° to 40° and cooling to 25°. After standing over night at 25° the specific conductivity at that temperature in two solutions was 0.002225 and 0.002227 respectively, indicating a concentration over 0.5 per cent. higher than that of the saturated solution. On revolving further, the conductivity became 0.002212 and 0.002215 respectively, identical with the result found by revolving at 25° continuously.

The solubilities are shown in Table I. Weighings are reduced to vacuum. Specific gravities are accurate to two or three units in the fifth decimal. Concentrations are in mols per liter.
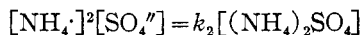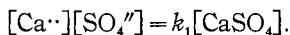
The calculated solubilities were derived by a series of approximations from the mass-law equations, k being furnished by the conductivity of the salt in the concentration involved; any dissociation of ammonium sulphate other than into $2NH_4$· and SO_4'' is disregarded.[2]   Symbols in brackets indicate concentrations:

[1] Anhydrous calcium sulphate obtained in this way or by addition of concentrated sulphuric acid and evaporation is not hygroscopic and may be exposed to the air indefinitely without change in weight, although the anhydrous salt which results from heating gypsum sufficiently to expel all water without loss of sulphur trioxide is, as is well known, hygroscopic. Furthermore, the anhydrous salt obtained by treatment with concentrated sulphuric acid gives off sulphur trioxide on heating less readily than does gypsum. This behavior is suggestive of a more intimate union with the water than is expressed by the formula $CaSO_4.2H_2O$. Compare the results obtained by Gooch and McClenahan, *Ztschr. anorg. Chem.*, **40**, 24 (1904), with metallic chlorides containing "water of crystallization."

[2] A. A. Noyes (*Phys. Rev.* **12**, 31 (1901) and *Ztschr. phys. Chem.*, **36**, 63 (1901)), concludes from the constancy of the transference number with varying concentration that in 0.1 molal potassium sulphate solution the concentration of KSO_4' ions, if they are present at all, does not exceed a very few percent of the total concentration. Kümmell (*Ztschr. Elektrochem.*, **9**, 975 (1903)) reaches a similar conclusion, on other grounds, with regard to magnesium chloride.

TABLE I.—SOLUBILITY OF CALCIUM SULPHATE IN AMMONIUM SULPHATE SOLUTIONS.

Concentration (NH₄)₂SO₄.	Mixture revolved, hours.	Grams CaSO₄ per 100 cc. found.	Means.	Concentration CaSO₄. Found.	Calculated.	Weight in grams of 1 cc. 25° C. Solvent.	Solution saturated with gypsum.
0.00	3 6½ 7	0.2085 0.2084 0.2081	0.2083	0.01530		0.99707	0.99911
0.0009766	I 6 II 16	0.2038 0.2047	0.2043	0.01500	0.0150	0.99711	0.99911
0.001953	I 4½ II 16½	0.1989 0.2004	0.1996	0.01466	0.0146	0.99721	0.99920
0.007812	I 6 II 16	0.1802 0.1812	0.1807	0.01327	0.0129	0.99765	0.99946
0.01563	I 3½ II 12	0.1651 0.1664	0.1658	0.01218	0.0113	0.99832	0.99995
0.03125	I 19 II 19	0.1536 0.1544	0.1540	0.01131	0.0099	0.99953	1.00104
0.06250	I 3 II 15	0.1440 0.1440	0.1440	0.01058	0.0088	1.00201	1.00341
0.1250	I 6 II 17	0.1453 0.1456	0.1455	0.01069	0.0081	1.00681	1.00817
0.2500	I 3 II 8	0.1617	0.1617	0.01187	0.0078	1.01606	1.01763
0.7500	I 5 II 10	0.2328 0.2331	0.2330	0.01712		1.05143	1.05344
1.500	I 4½ II 8½	0.3299 0.3360	0.3330	0.02446		1.10059	1.10324
3.000	I 4 II 8	0.4476 0.4523	0.4500	0.03305		1.18843	1.19149

$$[Ca^{..}][SO_4''] = k_1[CaSO_4].$$

$$[NH_4^.]^2[SO_4''] = k_2[(NH_4)_2SO_4]$$

The results calculated agree well with observation in the two most dilute solutions. From there on the solubility found is greater than calculated even in those dilutions in which the conductivity indicates absence of double salt.

Plotting the observed results and passing a curve through the points (Fig. 1) one notes a sharp decrease in solubility of gypsum with the first addition of ammonium sulphate. As the concentration of the latter increases (to about 0.02) the fall becomes more gradual, and the solubility passes through a minimum with about two-thirds of its original value when the concentration of ammonium sulphate is about 0.09 molal. From this point the solubility gradually rises, reaching the same value as in water for an ammonium sulphate concentration of about 0.6 molal; with 3 mols ammonium sulphate per liter over twice as much gypsum dissolves as in water. The curve is similar in form to that found by Cameron and Seidell[1] for calcium sulphate in sodium sulphate solution.

MacGregor[2] applies Arrhenius' principle of isohydric solutions to the calculation of the conductivity of mixtures, finding by a graphic method what isohydric solutions when brought together afford a mixture identical in composition with that under examination. The mixture is conceived as containing each electrolyte segregated in a definite portion of the volume of the solution, the solutions in these partial volumes being isohydric and their conductivity therefore not changed by mixing, i. e., the conductivity of the mixture is the mean of the conductivities of the components. With given quantities of salts and a given total volume to which they may be dissolved there is, in general, only one proportion in which the solvent may be divided between the salts to form isohydric solutions. By plotting the ion concentration as a function of the volume for the given quantity of each salt it may be found by inspection of the curves in what volumes the given quantities of salts must be dissolved in order that the solutions shall contain the common ion in identical concentration and that the sum of the volumes shall equal the volume of the mixture.

For example:

[1] *J. Phys. Chem.*, **5**, 643 (1901); Cameron and Breazeale: *J. Phys. Chem.*, **8**, 335 (1904).
[2] *Loc. cit.*
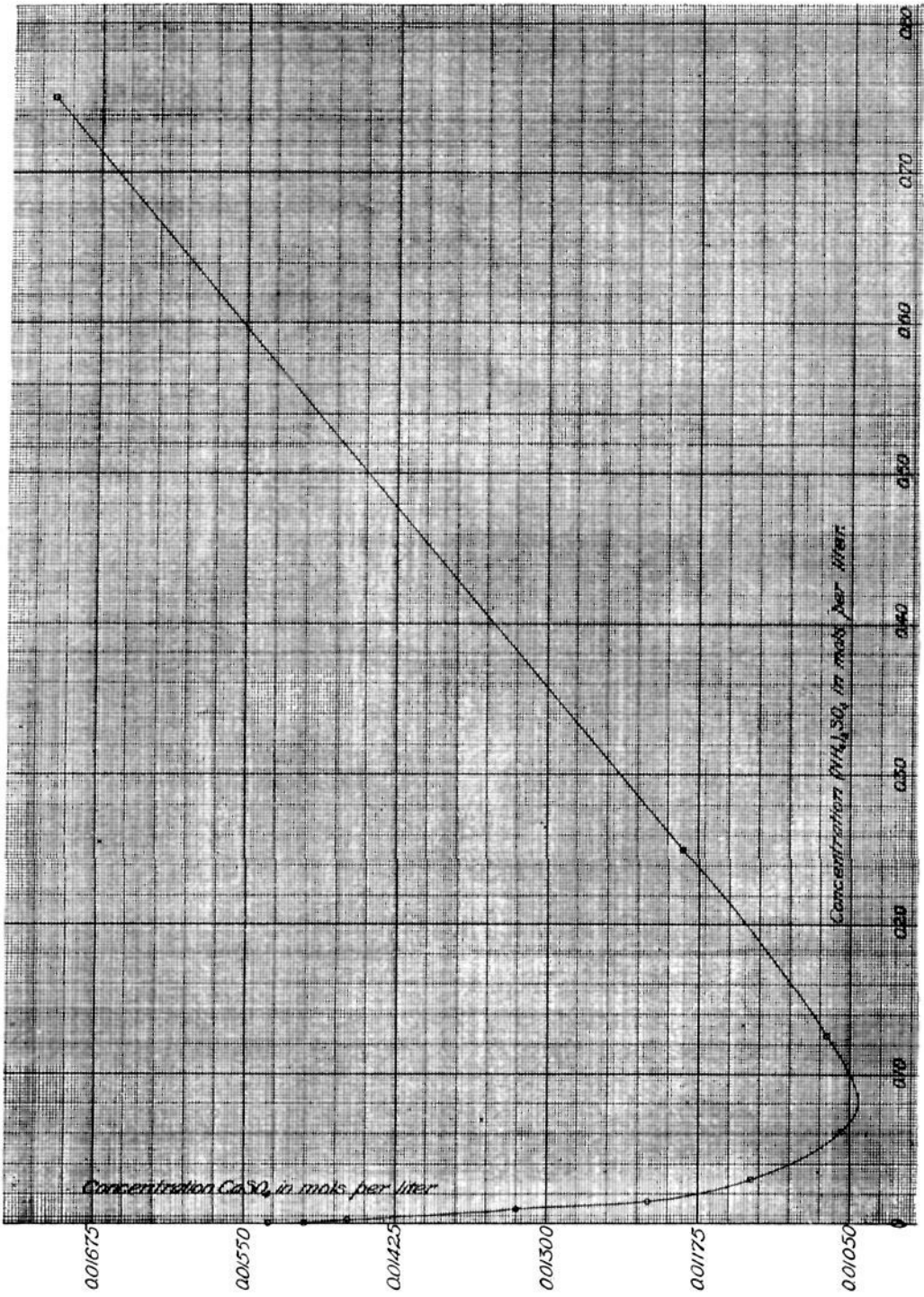
Solubility of gypsum in ammonium sulphate solutions.

1/1024 molal $(NH_4)_2SO_4$ (concentration $= 0.0009766$) dissolves gypsum in such quantity as to form 1/66.66 molal $CaSO_4$. To simplify calculation consider that quantity of this solution which contains one mol $CaSO_4$; we have then 66.66 liters of a mixture containing 33.33/512 mol $(NH_4)_2SO_4$ and one mol $CaSO_4$. What parts of this volume must be assigned respectively to these quantities of salts in order that the resulting solutions shall be isohydric?

Inspecting the curves (for $CaSO_4$ ion-concentration as function of the volume in which one mol is dissolved, for $(NH_4)_2SO_4$ ion-concentration as function of the volume in which 33.33/512 mol is dissolved), we find

1 mol $CaSO_4$ dissolved in 60.38 liters (spec. cond. 0.002346) and
33.33/512 mol $(NH_4)_2SO_4$ " " 6.28 " (" " 0.0002635)

Sum 66.66 "

contain the ion SO_4'' in like concentration (0.00848) and the sum of the volumes is identical with the volume of the original mixture.

On mixing such solutions each leaves the conductivity of the other undisturbed and the conductivity of the mixture is the sum of the specific conductivities multiplied by their respective volumes, the whole divided by the total volume:

$$0.002346 \times 60.38 = 0.1417$$
$$0.0002635 \times 6.28 = 0.0166$$

$$0.1583 \div 66.66 = 0.002375,$$

the calculated specific conductivity of the mixture.

The method in the hands of MacGregor and his associates[1] permits of the calculation of the conductivity of dilute mixtures—up to a concentration of about 0.25 mol per liter—with a mean deviation from the observed result at worst scarcely greater than the limit of error of an observation, which is estimated as 0.25 per cent. Na_2SO_4–K_2SO_4, K_2SO_4–$CuSO_4$, $ZnSO_4$–$CuSO_4$, NaCl–$BaCl_2$, K_2SO_4–$MgSO_4$ were among the mixtures examined.

Table II gives the results of the conductivity measurements for ammonium sulphate solutions saturated with gypsum. These were made, except in the concentrated solutions, in an Arrhenius cell with small electrodes. The more concentrated solutions were measured in a cell of inverted Y-shape, the electrodes fused into

[1] Archibald: *Trans. N. S. Inst. Sci.*, **9**, 291 (1897) and 307 (1898): McKay: *Ibid.*, 321 and 348 (1898).

the lower extremities. Bridge-wire and rheostat were calibrated. Temperature, $25°$ C.; conductivity corrected for slight variations. Specific conductivity is that of a cube of 1 cm. edge expressed in reciprocal ohms. Conductivity of the water used (1.7 to 3×10^{-6}) has been subtracted. Most of the results are the mean of at least two portions of the solution, several readings, at different points on the bridge-wire, having been made with each portion.

As Table II shows, the specific conductivity of ammonium sulphate in concentrations 0.75 and 1.5 is but little affected by saturating with calcium sulphate, while the conductivity of ammonium sulphate of concentration 3.0 saturated with calcium sulphate (conc. $= 0.033$) is about 1.5 per cent. *less* than that of the ammonium sulphate alone. The dilution due to water of the gypsum and expansion on dissolving the latter amounts to only about 0.2 per cent., so that the decrease in conductivity apparently is caused by the formation of complex ions having lower migration-velocity than those of ammonium sulphate. A blank experiment with concentrated ammonium sulphate solution and no gypsum showed no such falling-off in conductivity.

TABLE II.—CONDUCTIVITY OF AMMONIUM SULPHATE SOLUTIONS SATURATED WITH CALCIUM SULPHATE.

Concentration (a) $(NH_4)_2SO_4$ (b) $CaSO_4$.	Specific conductivity of single solutions.	Specific conductivity of mixture. Observed. Means.	Calculated by isohydric method.	Decrease if non-dissoc. $CaSO_4$ constant. Per cent.
(a) 0.000				
(b) 0.01530	0.002214			
(a) 0.000977	0.0002822	I 0.002391 } 0.002394	0.002375	0.2
(b) 0.01500		II 0.002397 }		
(a) 0.001953	0.0005475	I 0.002545 } 0.002546	0.002545	0.3
(b) 0.01466		II 0.002547 }		
(a) 0.007812	0.002025	I 0.003598 } 0.003602	0.003610	1.6
(b) 0.01327		II 0.003606 }		
(a) 0.01563	0.003801	I 0.005080 } 0.005085	0.005105	1.7
(b) 0.01218		II 0.005089 }		
(a) 0.03125	0.007083	I 0.008102 } 0.008106	0.00816	2.1
(b) 0.01131		II 0.008109 }		
(a) 0.0625	0.01306	I 0.01387 } 0.01388		
(b) 0.01058		II 0.01388 }		
(a) 0.1250	0.02391	I 0.02456 } 0.02457		
(b) 0.01069		II 0.02458 }		
(a) 0.2500	0.04332	I 0.04390 } 0.04389		
(b) 0.01187		II 0.04388 }		

Concentration (a) $(NH_4)_2SO_4$ (b) $CaSO_4$.	Specific conductivity of single solutions.	Specific conductivity of mixture.		Calculated by isohydric method.	Decrease if non-dissoc. $CaSO_4$ constant. Per cent.
		Observed.	Means.		
(a) 0.7500	0.1090	I 0.1091	} 0.1091		
(b) 0.01712		II 0.1091			
(a) 1.500	0.1853	I 0.1845	} 0.1846		
(b) 0.02446		II 0.1846			
(a) 3.000	0.2688	I 0.2653	} 0.2652		
(b) 0.03305		II 0.2650			

The Roman numerals refer to the solutions similarly designated in Table I.

In the table above we have the conductivity actually observed compared with that to be expected if Arrhenius' method of iso-hydric solutions is applicable. The close agreement[1] indicates that the mixtures have the composition assigned them in making the calculations by that method, presupposing always that conductivity is a measure of dissociation and that the latter takes place only into the ions here assumed.

The last column of the table shows the amount by which the conductivity of the mixture would be lower than that calculated, if the concentration of non-dissociated calcium sulphate were the same throughout as in the saturated water solution. The figures result from a comparison of the dissociation of calcium sulphate, as shown by Table IV, with the dissociation as obtained by subtracting the concentration of non-dissociated calcium sulphate in saturated water solution from the observed solubility in the several dilutions. Of the five mixtures for which this comparison can be made, in all but the two most dilute the difference seems to be outside the limits of possible errors of measurement and of method of calculation. It is to be concluded, then, that in these cases, the concentration of the non-dissociated portion of the calcium sulphate does not remain the same as in the saturated water solution.

Formation of complex compounds by union between ammonium sulphate and calcium sulphate would tend to lower the observed conductivity, acting therefore in the same direction as would constant concentration of non-dissociated calcium sulphate. The agreement between conductivity observed and calculated

[1] The fact that when two such electrolytes as calcium sulphate and ammonium sulphate are mixed each leaves the dissociation of the other unaffected is purely empirical; the mass-law would lead to the contrary expectation. Compare A. A. Noyes: *Tech. Quart.*, **17**, 302 (1904). This Journal, **27**, R. 201 (1905).

indicates that little or no such union takes place below concentration 0.0625. Measurements made under MacGregor's direction in one or two similar cases lead to the same conclusion.

The following data describe the isohydric solutions into which the mixtures are resolvable, and by means of which the conductivity was calculated :

<div align="center">TABLE III.</div>

<div align="center">Factitious isohydric solutions.</div>

Actual concentration $(NH_4)_2SO_4$.	Concentration SO_4''.	1 mol $CaSO_4$. Volume.	$(NH_4)_2SO_4$.	
			Mols.	Volume.
0.0009766	0.00848	60.38	$\dfrac{16.67}{256}$	6.28
0.001953	0.00897	56.24	$\dfrac{17.06}{128}$	12.00
0.007812	0.01229	37.84	$\dfrac{18.84}{32}$	37.52
c.01563	0.01700	25.08	$\dfrac{20.53}{16}$	57.0
0.03125	0.02675	15.24	$\dfrac{22.1}{8}$	73.2

The data for drawing the ion-concentration-volume curves were obtained in the case of calcium sulphate from as yet unpublished conductivity measurements on supersaturated gypsum solutions, very kindly placed at the writer's disposal by Dr. G. A. Hulett of the University of Michigan. The value for the most concentrated solution ($v = 15.24$) was derived by extrapolation, the curve embodying Hulett's observations terminating at $v = 17.64$. The results all lie almost absolutely on this curve, and are of sufficient number to make but slight interpolation necessary in getting at the values of the table above. For ammonium sulphate, the measurements detailed in Table II were used. Interpolation for other concentrations than those measured was made graphically, plotting molecular conductivity as function of cube root of dilution. This curve, drawn on a large scale by means of a spline, was tested by treating known points as unknown, and getting their value by interpolation. The results in the two trials made were but 0.3 per cent. from the correct values; the interpolations actually used in the calculations would be more accurate, as they were made through decidedly shorter intervals.

Molecular conductivity at infinite dilution, $25°$ C., was taken as 277 for calcium sulphate, 311 for ammonium sulphate.

The falling-off in concentration of non-dissociated calcium sulphate with increasing concentration of ammonium sulphate, is shown by the following table, which gives in mols per liter, the composition of the mixtures (saturated solutions) formed by the isohydric solutions of Table III :

TABLE IV.

Total concentration $(NH_4)_2SO_4$.	Concentration SO_4''.	Concentration Ca''.	Concentration non-dissociated $CaSO_4$.
0.00	0.0080	0.0080	0.0073
0.0009766	0.00848	0.00768	0.00732
0.001953	0.00897	0.00739	0.00727
0.007812	0.01229	0.00617	0.00710
0.01563	0.01700	0.00520	0.00699
0.03125	0.02675	0.00462	0.00620

SUMMARY.

Calcium sulphate, at 25° C., is two-thirds as soluble in dilute (0.1 mol per liter) and twice as soluble in concentrated (3 mols per liter) ammonium sulphate solution as in water.

The specific electric conductivity of concentrated ammonium sulphate solutions is lessened by saturating with calcium sulphate.

Assuming that dissociation of ammonium sulphate takes place into $2NH_4^{\cdot}$ and SO_4'' and of calcium sulphate into $Ca^{\cdot\cdot}$ and SO_4'' only, and that the conductivity is a measure of such dissociation, the solubility of calcium sulphate in dilute ammonium sulphate solutions is greater than required by the mass-law.

The conductivity of the dilute mixtures may be accurately calculated by means of Arrhenius' principle of isohydric solutions. In the data obtained in these calculations, the concentration of non-dissociated calcium sulphate decreases with increasing ammonium sulphate.

The work as a whole is additional evidence of the fact that we are not yet in possession of all the factors necessary for reconciling the mass-law to the behavior of electrolytes.

The measurements above described were made in the chemical laboratory of the University of Michigan.