Anal. Calcd. for $C_6H_7ON_3$: N, 30.6. Found: N, 30.1.

2-Amino-5-pyridinecarboxylic Acid (XIII).—Five grams of 2-amino-5-pyridinecarboxylic acid amide was suspended in 50 ml. of 10% sodium hydroxide solution and the mixture was refluxed until all the solid had gone into solution. After cooling, the solution was acidified with hydrochloric acid. The acid that precipitated in quantitative yield was almost pure and identical with that prepared according to Räth and Schiffmann[10] as shown by determination of a mixed melting point, m. p. 312°.

2-Amino-3-pyridinecarboxylic Acid Amide (XVIII).—To 12.5 g. of nicotinamide suspended in 50 ml. of pure dimethylaniline, was added 25 g. of finely pulverized sodium amide. The mixture was carefully heated in a metal bath to 140° (bath temp.) with vigorous mechanical stirring and in an atmosphere of nitrogen. Evolution of ammonia was quite vigorous when the temperature of the bath reached 100°, but it rapidly subsided and hydrogen was given off instead. Heating at 140–145° was continued for twelve hours. After cooling, the reaction mixture was cautiously diluted with 200 ml. of ice-water and the dimethylaniline was removed with several portions of petroleum ether (b. p. 35–60°). The aqueous layer was exactly neutralized with concentrated hydrochloric acid and allowed to stand in a refrigerator for 24 hours. The amide then was filtered off and recrystallized from aqueous alcohol, m. p. 195°; yield 20–25%.

The amide was hydrolyzed to the acid by a procedure analogous to that given above for its isomer and the acid was converted into the methyl ester according to Kirpal.[11] The m. p. of this ester (85°) was the same as that reported for methyl α-aminonicotinate by that author.

5-Nitro-2-pyridinesulfonyl Chloride (XX).—This compound was prepared from 5-nitro-2-pyridinethiol by a method analogous to that employed by Caldwell and Kornfeld[2] for the preparation of 5-acetylamino-2-pyridinesulfonyl chloride. After recrystallization from chloroform the compound melted at 212–213° (dec.).

Anal. Calcd. for $C_5H_3O_4N_2Cl$: Cl, 17.16; S, 15.51. Found: Cl, 16.93; S, 14.97.

Substituted Nitropyridine Sulfonamides, Acetaminopyridine Sulfonamides, and Acetylsulfanilamides.—One equivalent of 5-nitro-2-pyridinesulfonyl chloride or of 5-acetamino-2-pyridinesulfonyl chloride was added to one equivalent of the amine dissolved in four equivalents of pyridine, keeping the temperature of the solution below 50°. In those cases where the amine was not completely soluble in this quantity of solvent, enough dry acetone was added to get it completely into solution. The solutions were heated on the steam-bath for one hour and the derivatives were then precipitated by diluting with five volumes of water. The derivatives of acetylsulfanilyl chloride were prepared in the same way.

Substituted 2-Sulfonamido-5-aminopyridines.—Most of the acetyl compounds were hydrolyzed by refluxing 0.5 to 1.0 molar aqueous solutions containing 2.5 equivalents of sodium hydroxide for two hours. The derivatives of the dihalogenated aminopyridines were hydrolyzed in 50% aqueous alcohol solutions containing 2.5 equivalents of potassium hydroxide by boiling under reflux for fifteen to thirty minutes. In all cases the products were isolated by exactly neutralizing with concentrated hydrochloric acid and recrystallizing the precipitates formed from 60–80% acetic acid; yield 50–70%.

The nitro derivatives were reduced with sodium hydrosulfite in a way illustrated by the following example: 6 g. of 5-nitro-2-(N-5′-cyano-2′-pyridyl)-pyridinesulfonamide was suspended in 30 ml. of water containing 1.5 g. of sodium hydroxide, and 12 g. of sodium hydrosulfite was added with stirring while keeping the temperature below 50°. The amine was then obtained by neutralizing exactly with hydrochloric acid and recrystallizing the precipitate formed from aqueous alcohol; yield 30–40%.

Summary

1. A series of new substituted 2-sulfonamido-5-aminopyridines and two new derivatives of sulfanilamide have been prepared as indicated in the foregoing table.

2. Syntheses of new compounds, 5-nitro-2-pyridinesulfonyl chloride, 2-amino-3,5-diiodopyridine, 2-iodo-5-aminopyridine, and 2-amino-5-pyridinecarboxylic acid amide are described.

3. New procedures for preparing 2-amino-5-bromopyridine, 2-amino-5-cyanopyridine, 2-amino-3-pyridinecarboxylic acid amide, and 2-iodo-5-nitropyridine are given.

PHILADELPHIA, PA. RECEIVED MAY 18, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SOUTH DAKOTA STATE COLLEGE AND THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Behavior of Sulfur Dioxide as an Acid in Methanol

BY L. S. GUSS* AND I. M. KOLTHOFF

The acidity of aqueous solutions of sulfur dioxide is ordinarily attributed to the acids derived from sulfurous acid, H_2SO_3, HSO_3^- and H_3O^+. That H_2SO_3 is actually present in water solutions is evident from the work of Morgan and Maass,[1] Johnstone and Leppla,[2] Wright[3] and others. The first dissociation constant of the acid, 1.7×10^{-2}, refers to the total concentration of un-ionized sulfur dioxide. It is an apparent constant and the true constant of H_2SO_3 must be greater than this value, but is still unknown.

In the extended definition of Lewis,[4] sulfur dioxide exhibits an acidity itself without its having to react with a protolytic solvent like water. In other words, water solutions contain the protoacid,[5] SO_2, which should have acidic properties. Whether it can act as a "catalyst acid," for example in the inversion of sugar in aqueous medium, has apparently never been investigated. Lewis[4] states that sulfur dioxide in acetone as a solvent gives a bright red color with thymol blue and a more or less red color with butter yellow.

It is of interest to consider the solution of sulfur dioxide in anhydrous solvents, such as methanol. In the absence of water, sulfurous acid cannot be

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* Dr. L. S. Guss passed away on May 17, 1944.

(1) O. M. Morgan and O. Maass, *Can. J. Res.*, **5**, 162 (1931); see also W. B. Campbell and O. Maass, *ibid.*, **2**, 42 (1930).

(2) H. F. Johnstone and P. W. Leppla, THIS JOURNAL, **56**, 2233 (1934).

(3) R. Wright, *J. Chem. Soc.*, **105**, 2907 (1914).

(4) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(5) I. M. Kolthoff, *J. Phys. Chem.*, **48**, 51 (1944).

formed, yet solutions of sulfur dioxide in methanol are acidic. For example, the yellow color of thymol blue in methanol becomes red on the introduction of sulfur dioxide. This might be due to the interaction between the proto-acid, sulfur dioxide, with the indicator base, or to the formation of the addition compound CH_3OSO_2H, comparable to the formation of H_2SO_3 in water, or to both. There is no reference in the literature to the existence of the compound CH_3OSO_2H, although its sodium salt has been isolated.[6] It is known that sulfur dioxide forms an addition compound with methanol, but the latter is probably a simple solvate.[7]

From our work we conclude that solution of sulfur dioxide in methanol results in the formation of a monobasic acid

$$CH_3OH + SO_2 \rightleftarrows CH_3OSO_2H \rightleftarrows CH_3OSO_2^- + CH_3OH_2^+$$

In analogy with water solutions, there may be an equilibrium between CH_3OSOOH and CH_3OSO_2H, but this is of no consequence in the derivations made below.

We define a dissociation constant by the relation

$$\frac{a_{CH_3OSO_2^-}\, a_{CH_3OH_2^+}}{a_{SO_2}} = K_A \qquad (1)$$

This constant was evaluated colorimetrically with acid-base indicators and by conductance measurements of solutions of sulfur dioxide in methanol.

Experimental

Materials.—A good grade of absolute methanol was refluxed over magnesium ribbon, according to the method of Lund and Bjerrum.[8] After distillation, alkaline impurities were removed by refluxing with sulfanilic acid. The purity of the final product was checked with a 100-ml. pycnometer. No methanol was used whose density was less than 0.78661, which corresponds to a water content of 0.04%. Specific conductance determinations were made on all methanol used in conductivity work, no alcohol being used whose specific conductance was more than 2.0×10^{-7} ohm^{-1}.

Sulfur dioxide, from a tank, was washed successively through a barium chloride solution, concentrated sulfuric acid, a tube of cotton wool, and finally through pure methanol, before being bubbled into the methanol to be used in standard solutions. Solutions were standardized (a) by introducing a measured amount into excess iodine with shaking, and back titrating with standard thiosulfate, (b) by direct titration with an aqueous standard potassium iodate solution until the first appearance of a permanent brown color. Both methods gave consistent results, although the second is preferred because of its convenience.

Other solutions were prepared by methods previously described.[9] No solutions over a week old were used in any of the work reported. Sulfur dioxide solutions were always freshly prepared just before each determination, although no change was observed on standing, except for a slight decrease in concentration due to evaporation of the sulfur dioxide. Apparently, sulfur dioxide in methanol is not readily air-oxidized.

Procedure of Measurements.—Colorimetric measurements were carried out by the Gillespie method, described previously.[9] Comparisons were made in Pyrex glass test-tubes of uniform diameter, using a block colorimeter. The temperature was 25 ± 1°.

Conductance measurements were made in a Washburn cell, with polished platinum electrodes. A microphone hummer induction coil, frequency 10,000, served as source of alternating current, the system being balanced by the bridge of a simple Leeds and Northrup student type potentiometer. The cell constant was 0.216; temperature, 25 ± 0.1°.

Results

1. Colorimetric Study of Unbuffered Solutions.—In studying the equilibria of the reactions

$$I_b + CH_3OSO_2H \rightleftarrows I_a + CH_3OSO_2^-$$
$$I_b + CH_3OH_2^+ \rightleftarrows I_a + CH_3OH$$

(I_b denotes the basic form and I_a the acid form of the indicator), in solutions of sulfur dioxide in methanol with thymol blue as indicator, the use of isohydric indicator solutions was imperative. Most of our work was carried out with the conventional solutions of the sodium salt of thymol blue in methanol. Neglect of the use of isohydric indicator caused large errors. In the experiments reported in this paper, isohydric thymol blue was used in all cases.

The method of preparing isohydric indicator was similar to that of Kolthoff and Kameda.[10] A stock solution of thymol blue acid was prepared in methanol. This was divided into two equal parts. To one was added the calculated amount of sodium methoxide to yield the mono-sodium salt. To the other was added a volume of pure methanol equal to that added to the first solution. Mixtures of these two solutions were used in determining the acidity of the sulfur dioxide solutions. If the ratio of the two forms of the indicator remained unchanged when the concentration of indicator was doubled, it was assumed that the indicator was isohydric with the unknown solution.

Defining an indicator constant by the relation[9]

$$\frac{a_{CH_3OH_2^+}a_{I_b}}{a_{I_a}} = K_I \qquad (2)$$

we have, by combination with (1)

$$\frac{1}{a_{SO_2}}\left(\frac{a_{I_a}K_I}{a_{I_b}}\right)^2 = K_A \qquad (3)$$

In the unbuffered solutions of sulfur dioxide in methanol, the ionic strength is so low that activities may be set equal to concentrations. c_{SO_2} is taken equal to the stoichiometric concentration of sulfur dioxide. The value of K_I was previously found[9] to be 2.0×10^{-5}. In Table I are listed the data obtained in this colorimetric study.

The variation in values of K_A is within the experimental error in determinations of this kind. The average value of K_A is 3.8×10^{-7} or $pK_A = 6.42$.

2. Colorimetric Study of Buffered Solutions.—Since a methanol solution of sulfur dioxide behaves as a simple monobasic acid, a more accu-

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(6) Beilstein, "Handbuch der organischen Chemie," Vol. I, p. 282.

(7) G. Baumé and G. P. Pamfil, *J. chim. phys.*, **12**, 256 (1914).

(8) H. Lund and J. Bjerrum, *Ber.*, **64B**, 210 (1931).

(9) I. M. Kolthoff and L. S. Guss, THIS JOURNAL, **60**, 2516 (1938).

(10) I. M. Kolthoff and T. Kameda, *ibid.*, **53**, 821 (1931).

TABLE I

COLORIMETRIC DETERMINATION OF DISSOCIATION CONSTANT OF SULFUR DIOXIDE IN METHANOL WITH THYMOL BLUE

c_{SO_2}	$c_{I_b}:c_{I_a}$	$K_A \times 10^7$
0.00234	4:6	3.8
.00030	68:32	3.3
.00037	63:37	3.7
.00060	58:42	3.5
.000748	53:47	3.3
.000936	5:5	4.3
.00150	45:55	3.9
.00187	43:57	3.8
.00234	4:6	3.8
.00374	37:63	3.1
.00468	32:68	4.2
.00936	25:75	3.9
	Average	3.8×10^{-7}

rate determination of the dissociation constant can be obtained by a study of buffer solutions prepared by adding sodium methoxide to sulfur dioxide solutions. In the presence of thymol blue as indicator, we have

$$\frac{a_{I_b}a_A}{a_{I_a}a_B} = \frac{K_I}{K_A} \tag{4}$$

in which a_A is the activity of the acid form and a_B that of the basic form of the buffer. Knowing that $K_I = 2 \times 10^{-5}$, values of K_A are thus obtained. In buffer–indicator systems of the charge type used, it has been shown[9] that at moderate ionic strengths, concentrations may be used in place of activities. In Table II are listed some values of K_A obtained in this way.

TABLE II

COLORIMETRIC DETERMINATION OF DISSOCIATION CONSTANT OF SULFUR DIOXIDE IN METHANOL WITH THYMOL BLUE, IN THE PRESENCE OF SODIUM METHOXIDE

c_{SO_2}	c_{NaOCH_3}	$c_{I_b}:c_{I_a}$	$K_I:K_A$	$K_A \times 10^7$
0.108	0.0047	7:3	51	3.9
.108	.0024	6:4	66	3.0
.108	.00143	47:53	66	3.0
.108	.00095	35:65	61	3.3
.108	.00047	2:8	59	3.4
.0866	.00047	23:77	55	3.6
.054	.00047	38:62	70	2.9
.0433	.00047	4:6	62	3.2
.0325	.00047	47:53	62	3.2
.0216	.00047	57:43	61	3.3
		Average		3.3×10^{-7}

It is apparent that there is no appreciable variation of K_A with ionic strength. This is to be expected with a buffer–indicator system of the charge type used. The independence of K_A with sulfur dioxide concentration and the agreement of the value of K_A, 3.3×10^{-7}, with that obtained in unbuffered solutions, confirm the assumption that sulfur dioxide dissolved in methanol behaves like an ordinary (Brönsted) acid.

3. Effect of Water on Sulfur Dioxide Solutions in Methanol.

3. Effect of Water on Sulfur Dioxide Solutions in Methanol.—If some water is added to a methanol solution of sulfur dioxide, there is distribution of protons between the methanol and water.[11] The distribution is determined by the constant

$$a_{ROH_2^+}a_{H_2O}/a_{H_3O^+} = k = 0.23 \tag{5}$$

In other words, water in small concentrations acts as a base, and we have, essentially, a buffered system of the acid sulfur dioxide, and the base, water.

Assuming that the only action of the water is to lower the concentration of methanolium ions, we can combine (1), (2) and (5), giving us

$$\left(\frac{c_{I_b}}{c_{I_a}}\right)^2 = \frac{K_I^2\left(1 + \frac{c_{H_2O}}{k}\right)}{K_A c_{SO_2}} \tag{6}$$

If we plot $(c_{I_b}:c_{I_a})^2$ against c_{H_2O}, a straight line should be obtained whose slope is $K_I^2/kK_Ac_{SO_2}$. Knowing the values of k and K_I, K_A may be calculated. The data in Table III have been interpreted in this way.

TABLE III

EFFECT OF WATER ON THE COLOR OF THYMOL BLUE IN METHANOL SOLUTIONS OF SO_2

	$c_{SO_2} = 0.00250$		$c_{SO_2} = 0.00504$		$c_{SO_2} = 0.00756$	
c_{H_2O}	$c_{I_b}:c_{I_a}$	$(c_{I_b}:c_{I_a})^2$	$c_{I_b}:c_{I_a}$	$(c_{I_b}:c_{I_a})^2$	$c_{I_b}:c_{I_a}$	$(c_{I_b}:c_{I_a})^2$
0	5:5	1.00	38:63	0.37	32:68	0.22
.2	53:47	1.27	43:57	.57	35:65	.29
.4	57:43	1.75	48:52	.85	4:6	.43
.6	6:4	2.25	52:48	1.17	42:58	.52
.8	62:38	2.63	54:46	1.38	48:52	.85
1.0	67:33	4.12	57:43	1.76	5:5	1.00
1.2	68:32	4.50	58:42	1.91	5:5	1.00

These data are plotted in Fig. 1. Within the experimental error, there is a linear relation between $(c_{I_b}:c_{I_a})^2$ and c_{H_2O}. Taking K_I as 2×10^{-5}, we find the values of K_A as shown

Curve	c_{SO_2}	Slope	$K_A \times 10^7$
1	0.0025	2.26	3.1
2	.00504	1.38	2.5
3	.00756	0.70	3.4

The average value of $K_A = 3.0 \times 10^7$ is in satisfactory agreement with values obtained in the measurements in water-free systems.

4. Conductance Study of Methanol Solutions of Sulfur Dioxide.—In order to verify further the assumption that sulfur dioxide in methanol does not act partly as a "Lewis" acid, the dissociation constant was determined by the conventional conductance method. Elaborate care was not taken to prevent the loss of sulfur dioxide from the cell, although the conductance of a given solution was measured as soon as possible after its preparation. We have found by direct titration that there is little loss of sulfur dioxide from a methanol solution on short periods of exposure to air at moderate concentrations.

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[11] L. S. Guss and I. M. Kolthoff, THIS JOURNAL, **62**, 1494 (1940).

An examination of the conductance data of Goldschmidt[12] and Hartley[13] shows that for a large number of acids studied, the conductance at infinite dilution is equal to 200 ohms^{-1}, within 5%. In the calculations of Table IV, a value of 200 was taken for the equivalent conductance of CH_3OSO_2H in methanol.

TABLE IV

EQUIVALENT CONDUCTANCE OF METHANOL SOLUTIONS OF SO_2

c_{SO_2}	$k \times 10^6$	Λ	α	$K_A \times 10^7$
0.313	70.5	0.225	0.00112	3.9
.188	49.2	.262	.00131	3.1
.112	38.4	.342	.00171	3.3
.068	29.0	.427	.00213	3.1
.0415	22.5	.542	.00271	2.9
.0243	17.3	.713	.00356	3.1
.0146	13.0	.89	.00445	2.9
.0088	9.85	1.12	.00566	2.8
.00524	7.44	1.42	.0071	2.7
.00315	5.87	1.86	.0093	2.8
.00188	5.62	2.46	.0123	2.9
.00113	3.60	3.21	.0160	3.0
.00067	2.67	3.99	.0200	2.8

Within the limits of experimental error, the average value of $K_A = 3.0 \times 10^{-7}$ is in satisfactory agreement with values obtained by other methods.

Discussion

The apparent dissociation constant of sulfur dioxide from all the experiments is 3×10^{-7} or $pK_A = 6.5$. The corresponding value for the first dissociation constant in water is 2×10^{-2}. Hence, $pK_{A(M)} - pK_{A(W)} = 4.8$. This agrees fairly well with the change in dissociation constant of a monobasic acid as we go from water to methanol as a solvent.[9] This is rather an interesting coincidence, since both the dissociation constant of sulfur dioxide in water and that in methanol, are apparent constants. We conclude, therefore, that the reaction between water and sulfur dioxide to form sulfurous acid must be of the same order of magnitude as that between methanol and sulfur dioxide.

In its behavior toward the basic form of thymol blue, sulfur dioxide in methanol does not act like a Lewis acid. The reaction

$$I_b: + SO_2 \rightleftarrows I_b:SO_2$$

would represent a change from the basic to acidic form of thymol blue, brought about by the Lewis acidity of sulfur dioxide. This would be an interesting equilibrium to study, for it involves two forms of the indicator with the same charge type. The acidity of sulfur dioxide, in this sense, is so weak however, that its effect is completely masked in water or methanol by the stronger acids, H_2SO_3 and CH_3OSO_2H.

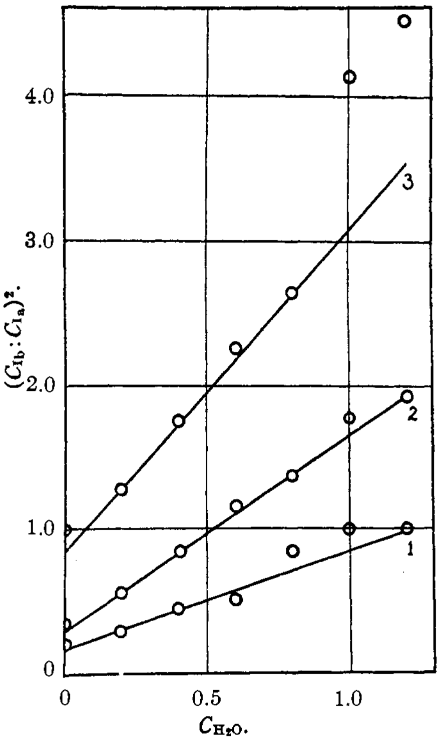

Fig. 1.—Effect of water on methanol solutions of sulfur dioxide.

The conclusion that sulfur dioxide in methanol behaves as a conventional acid is supported by the fact that the values of K_A calculated on this basis from colorimetric data seem to be independent of the sulfur dioxide concentration. Further, these values of K_A agree well with those obtained conductimetrically, the conductance being unaffected by a "Lewis" acidity of sulfur dioxide.

The acidity of methanol solutions of sulfur dioxide must be due, therefore, to the formation of the methyl ester of sulfurous acid

$$CH_3OH + SO_2 \rightleftarrows CH_3OSO_2H$$

a hypothetical substance which, like sulfurous acid, cannot be prepared as a pure compound. Its sodium salt is well known and is fairly stable, although it is decomposed by water.[6]

$$CH_3OSO_2Na + H_2O \longrightarrow CH_3OH + NaHSO_3$$

In low concentrations, the effect of water on methanol solutions of sulfur dioxide seems to simply result from the transfer of protons from methanol to water molecules. Thus in the presence of moderate concentrations of water, methyl bisulfite seems to be entirely stable.

The studies are being continued in methanol and ethanol as solvents.

Summary

1. The conventional dissociation constant of sulfur dioxide in methanol has been determined by colorimetric and conductimetric methods.

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[12] H. Goldschmidt and F. Aas, *Z. physik. Chem.*, **112**, 423 (1924); H. Goldschmidt and P. Dahl, *ibid.*, **114**, 1 (1924); H. Goldschmidt and E. Mathiesen, *ibid.*, **119**, 439 (1926).

[13] D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc.* (London), **A126**, 84 (1929).

2. The acidity of methanol solutions of sulfur dioxide is due to the monobasic acid, CH_3O-SO_2H, there being no indication of its acting as a "Lewis" acid with the basic form of thymol blue.

3. The addition of small quantities of water to methanol solutions of SO_2 results in the transfer of protons from methanol to water, without affecting other equilibria.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 15, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Conductance of Solutions of Magnesium Perchlorate in *n*-Propyl and Isopropyl Alcohols[1]

BY PIERRE VAN RYSSELBERGHE AND GILBERT J. HUNT

The high solubilities of several alkaline earth perchlorates in a number of organic solvents have been measured by Willard and Smith.[2] The possibility of studying concentrated organic solutions of such salts is of very great interest from the point of view of the general theory of electrolytic solutions. Investigations on organic solutions of magnesium perchlorate are being carried out in this Laboratory. The conductances of aqueous solutions of this salt at 25°, heretofore missing, were recently reported by Van Rysselberghe and McGee.[3] In the present paper we report the conductances of solutions of magnesium perchlorate in *n*-propyl and isopropyl alcohols at 25°.

Experimental

Magnesium Perchlorate.—The complete dehydration of magnesium perchlorate requires extreme care. The method finally adopted was the following: the commercial G. F. Smith product ("anhydrone") or Eastman Kodak Co. white label magnesium perchlorate was changed into the hexahydrate, which was recrystallized. This salt was transferred to a quartz tube electrically heated in steps to 245° and kept at that temperature for ten hours, in vacuum (magnesium perchlorate decomposes at 250°). The dehydrated product was kept over phosphorus pentoxide. Its purity was repeatedly checked by analysis.

***n*-Propyl Alcohol.**—Eastman Kodak Co. white label *n*-propyl alcohol was refluxed for five hours over calcium oxide. The 95–98° fraction was collected by distillation from the calcium oxide and was then carefully fractionated. The specific conductance of the solvent used in the preparation of the solutions was found to be $8 \cdot 10^{-8}$ mho, in exact agreement with the value given by Scudder.[4]

Isopropyl Alcohol.—Eastman white label isopropyl alcohol was refluxed for five hours over calcium oxide. The 81–83° fraction was collected by distillation from the calcium oxide and was then carefully fractionated. The specific conductance of the solvent used in the preparation of the solutions was found to be $4 \cdot 10^{-6}$ mho, in close agreement with Scudder's value.[4]

Conductivity Bridge.—A Jones bridge of the Leeds and Northrup Company was used for all the conductance measurements. The 1000 cycle alternating current was provided by a R. C. A. beat-frequency audio oscillator and the current in the telephone receiver was amplified by means of a specially-built two-stage audio-frequency amplifier.

Conductivity Cells.—Two Jones cells of the Leeds and Northrup Company were used (constants, 9.179 and 0.2744). Concordant results were obtained with an older type of cell with spongy platinum electrodes (constant, 13.242).

Temperature Control.—An oil thermostat kept at 25 ± 0.005° by means of a toluene regulator and an electronic relay was used.

Preparation of Solutions.—Several series of solutions were prepared by successive dilutions, these dilutions being carried out on a weight basis, with the usual buoyancy corrections. The concentrations in the various series were made to overlap to a certain extent and the agreement of the conductivities so obtained was our main criterion of accuracy. Close checks were obtained with samples of salt and solvents prepared at distant intervals of time. Errors due to impurities, water in particular, have no doubt been reduced to a strict minimum.

TABLE I

CONDUCTANCE OF SOLUTIONS OF MAGNESIUM PERCHLORATE IN *n*-PROPYL ALCOHOL AT 25°

Concn. equiv. per liter	Sp. cond. mhos $\times 10^4$	Equivalent conductance
0.0000000	0.00000	25.75
.0001814	.03647	20.105
.0004950	.08198	16.562
.001727	.1857	10.753
.003748	.2895	7.723
.005804	.3620	6.239
.009888	.5904	5.971
.01240	.6562	5.292
.01510	.6970	4.616
.02562	1.132	4.419
.03245	1.296	3.994
.04318	1.616	3.748
.05117	1.718	3.357
.05200	1.721	3.310
.08833	2.689	3.044
.1195	3.417	2.859
.1351	3.731	2.762
.1766	4.532	2.566
.2408	5.592	2.322
.2696	6.188	2.295
.4952	9.524	1.923
.5372	10.39	1.914
.8567	15.37	1.794
1.0703	18.02	1.684
1.128	18.69	1.659

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(1) From a thesis submitted by Gilbert J. Hunt in partial fulfillment of the requirements for the M.A. degree at the University of Oregon, June, 1944.

(2) H. H. Willard and G. F. Smith, THIS JOURNAL, **45**, 286 (1923).

(3) P. Van Rysselberghe and J. M. McGee, THIS JOURNAL, **65**, 737 (1943).

(4) H. Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, N. Y., 1914.