ABSOLUTE SULPHURIC ACID: ITS PREPARATION FROM SULPHUR TRIOXIDE AND WATER; ITS SPECIFIC ELECTRIC CONDUCTIVITY AND THAT OF MORE DILUTE ACID.

BY D. M. LICHTY.

Received September 15, 1908.

My special interest in the properties of concentrated sulphuric acid dates from the time of my study of the decomposition in it of anhydrous oxalic acid.[1] The speed of the decomposition was surprisingly decreased[2] by the addition of only 0.01 per cent. of water to a supposedly 100 per cent. acid.[3] Since the most exact gravimetric or volumetric analysis of concentrated sulphuric acid is subject to an error whose magnitude is considerably over 0.01 per cent.,[4] different samples of acid, which, according to either method of analysis had the same concentration, could not on that account alone be expected to yield, and as a matter of experience did not yield the same constants for the speed of decomposition of oxalic acid. Although samples of acid, which possessed the same specific conductivity for electricity, yielded concordant constants, yet, since the exact conductivity of any one concentration of concentrated acid was unknown, this method could not serve to establish the composition of the acid used.

If so-called absolute sulphuric acid is really a definite substance, whose composition is expressed by the formula H_2SO_4, then an acid containing a larger percentage of either sulphur trioxide or water than is represented by this formula would be a solution. The absolute acid should then exhibit the maximum freezing point. This would also be true even if sulphuric acid is partly dissociated, say into trioxide and water, provided that the concentration of the products of dissociation reaches its minimum at 100 per cent. An absolute acid could then be prepared by adding sulphur trioxide to very concentrated acid or water to slightly fuming acid, until the maximum freezing point is reached. Dr. R. Knietsch, in 1905,[5] expressed it as his belief that the measurement of the freezing point of very concentrated sulphuric acid is a very exact method for determining its composition.

Marignac[6] showed that the highest boiling point of sulphuric acid does not belong to 100 per cent. acid, but to one whose concentration is about 98.5 per cent. He also observed that a 100 per cent. acid gives out anhydride when heated to only 30–40°. The first observation, con

---

[1] *J. Phys. Chem.*, 11, 225 (1907).
[2] *Ibid.*, p. 250, Table 24.
[3] *Ibid.*, pp. 338–40.
[4] Domke and Bein, *Z. anorg. Chem.*, 43, 126–7 and 132 (1905).
[5] Private communication to Prof. Bredig, Heidelberg.
[6] *Ann. chim. phys.*, 39, 189 and 192 (1853).

firmed by Dittmar[1] and by Pfaundler,[2] indicates beyond a doubt that, at a temperature approaching its boiling point, sulphuric acid dissociates into water and sulphur trioxide. Since the methods of analysis used by Marignac would not enable him to distinguish between an absolute acid and one which contained a slight excess of anhydride, the second observation still leaves it in doubt whether or not sulphuric acid is dissociated into water and anhydride at low temperatures. The result obtained by Pfaundler,[3] namely, that by passing dry air through slightly fuming acid at 16–19° under atmospheric pressure until no further change in composition occurs, there was left a liquid which was equivalent to 100.08 per cent. sulphuric acid, would indicate that in this temperature interval there is no dissociation of sulphuric acid into water and anhydride. His analyses were also subject however to the not inconsiderable error already mentioned.

In view of these uncertainties it appeared worth while to attempt the preparation of absolute sulphuric acid by mixing pure water and pure sulphur trioxide in stoichiometrical proportions. Sufficiently pure water could readily be obtained, so that the principal problem consisted in obtaining pure sulphur trioxide and in preventing it from absorbing moisture while it was being transferred to a weighing vessel, or otherwise handled.

Preparation of Anhydrous Sulphur Trioxide.—For the preparation of pure anhydrous sulphur trioxide, a method was used which is similar to that employed by Weber.[4] Since the evidence that the sulphur trioxide was obtained in a pure state, rests largely in the method used, the latter will be given at some length.

In the asbestoslike, or polymerized[5] state, the form in which sulphur trioxide is readily obtainable on the market, it is not easily manipulated, being difficult to melt so as to be successfully transferred to a distilling apparatus, or becoming so hard when exposed to moist air as to make transference no less difficult. When obtained in glass-stoppered bottles rather than in sealed bulbs, the transference to a distilling flask is readily accom-

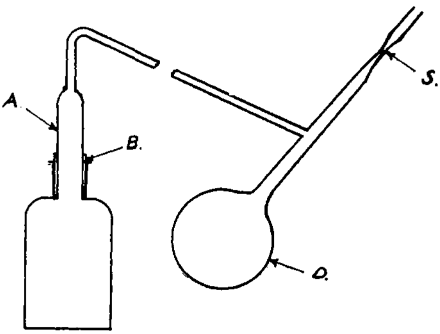

Fig. 1.

---

[1] *Z. für Chemie*, 13, 1 (1870).

[2] *Ibid.*, p. 66.

[3] *Loc. cit.* See also Lidbury, *Z. physik. Chem.*, 39, 467 (1902).

[4] *Pogg. Ann.*, 159, 313 (1876); *Ber.*, 19, 3187 (1886); see also Schenk, *Ann.*, 316, 1 (1901).

[5] Oddo, *Gazz. chim. ital.*, 31, II, 158 (1901).

plished with an apparatus like that depicted in Fig. 1. *A* is a glass adapter; *B* a winding of sheet asbestos for making a loose-fitting joint between the end of *A* and the neck of the bottle; *D* a fractionating flask with a constricted tube sealed to its neck. The space between *B* and the neck of the bottle was tightly packed with fine asbestos, such as is used in making filters. Then the projecting portion of *B* was torn away and the asbestos covered with a thick layer of sealing wax. When the latter was cold, the apparatus was exhausted to about 30 mm. pressure and finally sealed at *S*. If, after a test applied in the course of several hours, the joint at *B* was found to be air-tight, the distillation could be undertaken without any danger that the internal pressure would become high enough to cause an explosion, provided of course that the heating of the bottle and the cooling of the receiver were both properly conducted. The bottle was placed on a water bath whose temperature was very gradually raised to the boiling point. The receiver *D* was cooled in a rapid stream of water at 10–15°. In this way portions of 600–700 grams of sulphur trioxide were transferred to a distilling flask in the course of about 8 hours, without bringing the interval pressure higher than that of the vapor of liquid trioxide at 35°, *i. e.*, at 10° below its boiling point under one atmosphere.

After the transfer was accomplished the distilling flask was opened at *S* and then disconnected from the bottle by breaking or sealing off the tube which joined it to the adapter. To the side arm of the distilling flask there were now sealed two smaller flasks, connected at right angles to each other with 30–40 cm. of tubing, the two legs of the right angle being placed in a nearly vertical plane, and the connection with the distilling flask being made at the right angle, Fig. 2. The upper, larger of the two small flasks had previously been charged with about 10 grams of pure phosphorus pentoxide,[1] and had a tube, bearing numerous constrictions, sealed into its stem so as to stand in about the same plane as the legs of the right angle, Fig. 2. The purpose of the stopper *C* will be made plain by Fig. 4 and the description accompanying it.

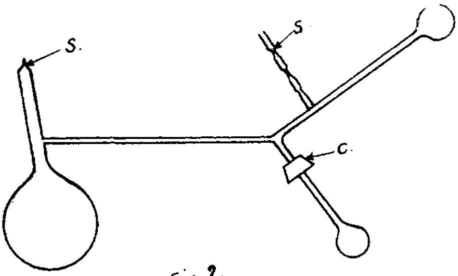

Fig 2.

After sealing at *S* and opening at *S′*, the apparatus was exhausted to about 30 mm. and sealed. Under the conditions above given, there was then distilled into the lower flask a quantity of trioxide sufficient to

---

[1] The supply bottle bore Kahlbaum's label, and a sample gave a barely recognizable coloration with ammoniacal silver nitrate solution.

about fill it (150–180 grams), the condensation of distillate in the upper flask being prevented by warming it. Air, which was dried by means of sulphuric acid and phosphorus pentoxide, was now admitted at *S′*, the distilling flask sealed off as near the right angle as convenient, the two small flasks exhausted to about 30 mm. and sealed, thus constituting the apparatus for the final dehydration of the sulphur trioxide.

As there was always moisture introduced into the apparatus when its parts were finally sealed together, the distillate, collected as above described, was always polymerized to such an extent by the resulting sulphuric acid that only by immersing the containing flask in boiling water and heating it there for an hour and often longer could the charge collected be completely distilled over upon the phosphorus pentoxide. The next step consisted in removing the traces of sulphuric acid from the receiver, by rinsing it repeatedly with 5–10 cc. of distillate. Even these small portions could not at first be collected without quickly polymerizing, unless only moderate cooling was applied. If a nodule of polymer appeared, it was at once loosened from the receiver wall by gentle warming, and rinsed into the distilling flask. This polymerization was one of the most troublesome features of the work. Usually after about six rinsings the entire charge of the apparatus could be distilled without showing any polymerization. As soon as this could be done the distillate was frozen by cooling below 16°. Even if, after standing some hours in this state, no polymerization set in, the distillation was repeated four to six times as an extra precaution to secure thorough dehydration.

Before severing the receiver with its contents from the distilling flask, the stopper *C* was pushed as close to the receiving flask as possible, then air, dried by passing through three bottles of sulphuric acid and a 25 cm. column of pumice stone and phosphorus pentoxide, was slowly admitted at *S′*, through a thick-walled and securely wired rubber tube, until a pressure slightly in excess of one atmosphere was reached. The drying apparatus was at once disconnected and the receiver quickly sealed off in such a way as to leave connected with it about 15 cm. of tubing with its sealed end turned at a right angle[1] to the axis of the tube. As many as six large samples of sulphur trioxide were prepared in this way. In the angle of the sealed end of each container, there appeared after a time a larger or smaller quantity of polymer, while the main mass in the bulb remained unpolymerized, even though it was repeatedly frozen.

In no case did the air space over the trioxide exceed 15 cc. This volume of air at 20°, if saturated with water vapor, would contain less than 0.3 mg. of water. After it was dried in the way stated, the amount of water in it must have been much smaller, and yet it was sufficient to induce some polymerization!

[1] Object shown in Fig. 4 and the description accompanying it.

Transferring to a Weighing Vessel.—For this purpose large test tubes, 40 mm. in diameter, were used. Each was constricted to about 10 mm., at a point far enough from the sealed end to furnish a container with a capacity about 1.5 times as large as the volume of trioxide to be introduced. After cleansing, steaming and drying, the adsorbed moisture was removed by passing a stream of air, dried as stated above, through each for 30 to 40 minutes, while it was being kept at a temperature at which it turned a Bunsen flame bright yellow. Subsequently, the tube was cooled slowly enough to permit the inflowing dry air to maintain in it a slight pressure, Fig. 3.

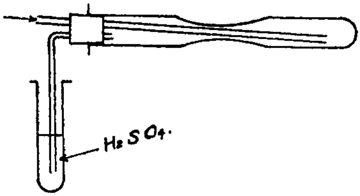

Fig. 3.

After being provided with a wire hanger, the tube was now brought to the temperature of the balance room, disconnected from the drying apparatus, covered with a glass cap and weighed. All weighings were made with a set of carefully calibrated weights.

The tube was now ready for the transfer which was carried out by the arrangement shown in Fig. 4. The rubber stopper is the one shown in Fig. 2. Its end was covered with a disc of ignited asbestos to prevent it from contaminating the sulphur trioxide. Air was passed through the tube exactly as before, and when it was cooled, but the air still flowing, the tube *T* was drawn back so that its end was about on a level with the sealed end of the trioxide bulb. The connection at *C* was then severed, and the apparatus reversed. The tip of the trioxide bulb, which, to prevent it from falling into the tube below, had previously been fastened to a platinum wire extending out through *W*, was broken off by pressing on it with the end of *T*. By carefully warming the bulb *B*, the sulphur trioxide was now expelled into the tube. The latter was immersed in ice water, and, as soon as the transfer was completed, was sealed off at the constriction. What weighings were still necessary to finally secure the weight of the trioxide will be readily understood. In spite of this careful exclusion of all water, except such traces as must have been negligible in comparison with the weight of sulphur trioxide used, there was still sufficient present to cause slight fuming when the trioxide flowed into the weighing tube, and to cause some polymerization when the trioxide was cold.

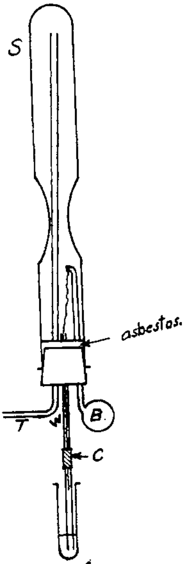

Fig. 4.

Mixing the Water and Sulphur Trioxide.—Since the specific gravity of sulphur trioxide at 20° is about 1.9,[1] its apparent weight was corrected to a vacuum by multiplying by 1.0005.[2] In calculating the weight of water needed, the molecular weights of sulphur trioxide and water were taken as 80.06 and 18.016 respectively. From the weight of the water in a vacuum, its apparent weight was found by dividing by 1.00106.[2] In each case the weight of water used differed from the calculated weight by only ±1 mg.

The mixing of the sulphur trioxide and the water, which probably constituted the most dangerous part of this research, was successfully accomplished with three samples while two were lost by accidents. One of the accidents was caused by the too rapid mixing of the two liquids, and was accompanied by a terrific explosion. The method followed will be made plain by the help of Fig. 5, in which *S* is a tube 35–40 cm. in length with walls of medium thickness; *A*, a piece of glass rod with rounded ends; *B*, a very thin-walled bulb containing the water; *C*, the bulb with the sulphur trioxide; *D*, pieces of thick-walled glass tubing. Each article contained in *S* was previously cleaned and then dried, finally in a desiccator over sulphuric acid. The outer tube had been dried and filled with dry air.

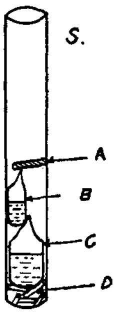

Fig. 5.

After sealing at *S*, the bulb *B* was broken by means of *A*, while the space in the tubes *D* permitted the water to flow below *C*. This left *C* entirely above the water, and made it possible to break off its point with *A*, without bringing the trioxide and water together in the liquid state. To prevent *C* from sliding up and then falling back on *D* and breaking at the bottom, during the attempt to break off its tip, the apparatus was laid in an inclined position into a freezing mixture and *C* frozen securely to the outer tube. When the opening in *C* was large enough to admit A, the tube was set aside until the upper portion of the trioxide had become well polymerized, then by inclining it carefully, water was introduced into *C*, little by little, until most of the trioxide had disappeared. To readily permit obtaining a homogeneous product, the bottom was then broken out of *C*.

Specific Conductivity.—The specific electrical conductivities, which will be more fully discussed in the next division, were found to be as follows, at 25.00°:

For product 1	0.01044	reciprocal ohms.
" " 2	0.01042	" "
" " 3	0.01042	" "

---

[1] R. Schenck, *Ann.*, 316, 14 (1901).

[2] Ostwald-Luther, *Phys.-Chem. Mess.*, **1902**, p. 53.

The mean of these three values, then gives 0.01043 reciprocal ohms as the specific conductivity of absolute sulphuric acid.

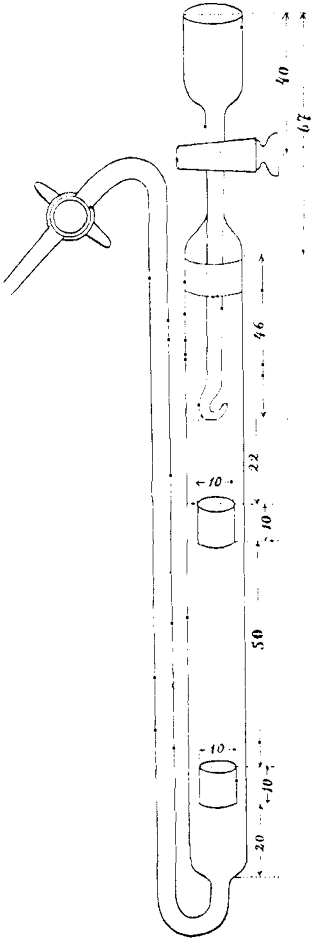

Fig. 6.

Later 2 and 3 were mixed and to a little more than 100 grams of the mixture a trace over 0.01 per cent. of water was added. This raised the conductivity to 0.01071. To a second portion, this time about 125 grams, of the mixture of 2 and 3, there was added enough fuming acid (15.5 per cent. of free SO_3) to leave about 0.02 per cent. of free sulphur trioxide (equivalent to less than 0.004 per cent. of water). This raised the conductivity to 0.0105.

To determine how near the mean specific conductivity, found for the three samples of absolute sulphuric acid, lies to the minimum conductivity of concentrated sulphuric acid, a slightly fuming acid (about 0.7 per cent. of free SO_3) was prepared and its conductivity measured.

To this was then added 90 per cent. acid, drop by drop, and a measurement made after the addition of each drop. The form of cell used for all the measurements is shown in Fig. 6. To mix the acids thoroughly, 25–30 bubbles of air, dried with phosphorus pentoxide, were drawn through the cell. A few blank tests with altogether several hundred bubbles of dried air, did not introduce enough moisture to affect the conductivity of the acid. The result of the measurements is given in the adjoining table.

90 per cent. acid added.	Conductivity.
0 drop	0.01111
1 "	0.01069
2 "	0.01058
3 "	0.01041
4 "	0.01048
5 "	0.01075
7 "	0.01184

To the now slightly aqueous acid, enough of the fuming acid was added to introduce a slight excess of anhydride, then 96 per cent. acid was added drop by drop and measurements made as before, the 96 per cent. acid being added so as to make the successive additions of water very small. This process was repeated four times. In four cases the minimum value found was exactly 0.01041, in one case two successive values of 0.01042, between which the minimum must have been passed. The minimum specific conductivity of concentrated sulphuric acid, as here found in six measurements, is then 0.01041 reciprocal ohms, a value from which the mean specific conductivity of absolute sulphuric acid above found, differs only by 2 units in the fourth significant place and from which the value found for samples 2 and 3 differ by only one such unit.

The mean of three measurements of the conductivity of the sulphuric acid used in the work on oxalic acid[1] (0.01043, 0.01043, 0.01037) is also 0.01041, indicating that that acid was what it was assumed to be, *i. e.*, 100 per cent. Since an increase in the conductivity from 0.01041 to 0.01068,[2] *i. e.*, one of 0.00027, was caused by the addition of but 0.01 per cent. of water, the conductivity, 0.01044 of sample 1 of absolute acid, would have required the presence of an excess of only 0.001 per cent. of water. For the preparation of sample 1, 94.228 grams of sulphur trioxide were used, and should have yielded 115.41 grams of absolute acid, 0.001 per cent. of which is less than 1.2 mg. The deviation of the conductivity of sample 1 from the minimum could then have been caused by about 1 mg. excess of water.

When the conductivity measurements just described had been completed, 82 grams of sample 1, and 103 grams of the mixture of 2 and 3 were each diluted with about 2 volumes of water. To learn whether any sulphurous acid, phosphorous acid or other oxidizable substance was present, each portion was treated, while warm, with approximately 0.25 *N* bromine water. With the addition of each drop, the practically colorless solution grew deeper in color, indicating freedom from reducing material. The bromine disappeared only on being boiled out of the solution. When this had been done, each was concentrated in a platinum dish over a water bath and finally evaporated carefully to dryness over a free flame. From 1, there was left a residue representing a trifle over 0.003 per cent. of the original, while from the mixture of 2 and 3, there was left one of less than 0.002 per cent. A portion of each was soluble in dilute hydrochloric acid and with ammonium molybdate and nitric acid gave a test for phosphoric acid. The rest was insoluble and consisted of glass dust introduced, during their preparation, when the water and sulphur trioxide bulbs were broken.

That these traces of impurity had no measurable effect on the con-

---

[1] *J. Phys. Chem.*, 11, 240 (1907).

[2] *Ibid.*, p. 264.

ductivity, is shown by the fact that the minimum conductivity of an acid prepared from pure 96 per cent. acid and trioxide, which was free from all impurities except sulphuric acid, was also 0.01041.

It may then be stated without hesitation, that the minimum specific electrical conductivity of concentrated sulphuric acid is the specific conductivity of the absolute acid.

Knietsch[1] found the minimum conductivity at 99.9 and 99.95 per cent., while W. Kohlrausch[2] found it at 99.74–99.75 per cent. The deviations from 100 per cent. found by these two investigators, are in all probability due to analytical errors.

A. Hantzsch,[3] and Oddo and Scandola,[4] in publications which came to my notice after the above results were obtained, state that they have based the preparation of absolute sulphuric acid upon the maximum freezing point. In view of what is said on this point on pp. 1834 and 1835, this procedure was based on an assumption, not by any means entirely unwarranted, however, as is shown especially by the behavior of sulphuric acid as found by Hantzsch.

I found that the addition of either 96 per cent. acid or of fuming acid to absolute sulphuric acid depresses the freezing point. The maximum freezing point of concentrated sulphuric acid is then the freezing point of the absolute acid. The value found is 10.43°–10.45°.[5] Then both the minimum specific conductivity and the maximum freezing point belong to absolute sulphuric acid. Hantzsch[6] likewise found that the sulphuric acid which possesses the maximum freezing point also possesses the minimum specific conductivity. The values which he found for the latter, 0.0097–98 with one cell and 0.0101 with another, are appreciably lower than the one found by me.

Conductivity of Absolute and of Slightly Diluted Sulphuric Acid.—The measuring cell (Fig. 6) showed practically the same resistance capacity (3.164 and 3.166) with two entirely different and thoroughly purified samples of potassium chloride. The solutions were made as directed in Ostwald-Luther,[7] and were 0.1 *N*. In addition to the specific conductivity of absolute sulphuric acid, that of each of a number of somewhat diluted acids was also measured. Several kilograms of slightly fuming acid, made from pure 96 per cent. acid and distilled sulphur trioxide, were brought to the minimum conductivity by the addition of 96 per cent. acid. The proportion of the latter needed to attain the minimum (also found at

---

[1] *Ber.*, **34**, 4107–8 (1901).

[2] *Wied. Ann.*, **17**, 69 (1882).

[3] *Z. physik. Chem.*, **61**, 258 (1907).

[4] *Ibid.*, **62**, 245–9 (1908).

[5] Hantzsch found 10.46°, Oddo and Scandola 10.43°.

[6] *Loc. cit.*

[7] *Phys-chem. Mess., Auf.*, p. 407.

0.01041) was found by diluting a known weight of the slightly fuming acid, in the measuring cell, drop by drop, with 96 per cent. acid, the weight of a few hundred drops of which had been previously determined. By adding the necessary weights of water to portions of this absolute acid, there were prepared mixtures, containing the percentages of water stated in the first column of Table I. In the second column of the table are given the conductivities of these mixtures. The third column contains the conductivities of like mixtures, measured when the work on oxalic acid was done. The two series are, in general, in good agreement. Column 5 shows that according to the results obtained, the successive increments in the conductivity take place somewhat irregularly.

TABLE I.

Per cent. of water.	Specific conductivity found.		Means.	Successive increments in hundred thousandths.
0.00	0.01041	0.01041	0.01041	..
0.01	0.01066	0.01068	0.01067	26
0.02	0.01091	0.01080	0.01085	18
0.03	0.01146	0.01122	0.01134	49
0.04	0.01163	0.01171	0.01167	33
0.05	0.01212	0.01210	0.01211	44
0.07	0.01349	0.01352	0.01350	70
0.10	0.01572	0.01560	0.01566	72
0.15	....	0.01998	0.01998	86
0.20	0.02389	0.02404	0.02396	80
0.30	0.03090	0.03128[1]	0.03109	77
0.40	....	0.03768[1]	0.03768	66
0.50	0.04287	0.04316[1]	0.04301	53
0.70	0.05272	0.05308[1]	0.05290	49
1.00	0.06430	0.06438[1]	0.06434	38
1.50	0.07949	0.07929	0.07939	30
2.00	0.09057	0.09101	0.09079	22
3.00	0.1068	0.1069	0.1068	16
4.00	0.1176	0.1181	0.1178	11
6.00	0.1292	0.1293	0.1292	6
8.00	0.1330	0.1328	0.1329	2
10.00	0.1299	0.1300	0.1299	..

In Table II, column 3 brings out the irregularities more clearly. Since they do not cause a sharp break in the curve (Plate I) it seems fair to assume that they are the result of experimental errors; *i. e.*, that the conductivity changes more regularly. With the view of obtaining for the conductivity, values which change more regularly and yet do not differ much from the means found, the experimental errors were distributed so as to yield the series of increments recorded in column 4. The regularity of their change is seen by their differences, given in column 5. The con-

---

[1] Calculated from the conductivity found on adding 0.3, 0.4, 0.5, 0.7 and 1.0 part of water respectively to 100 of absolute acid. *J. Phys. Chem.*, **11**, 264.

ductivities, based on what may be called these idealized increments, are given in column 6, and do not differ appreciably from those found by measurement, except in the three marked with an asterisk, and even here not seriously. For a water content up to 2 per cent., the increment in the specific conductivity per increment of 0.01 per cent. of water, lies between 16 and 87. These differences are ample to easily permit the determination of the sulphuric acid content to less than 0.01 per cent. If the amount of water in the acid is 3 or 4 or possibly 5 per cent., the differences in conductivity will permit the determination of the acid to 0.01 per cent. For less concentrated acids, the error is larger than 0.01 per cent., but up to 8 per cent. of water, it is probably within 0.1 per cent.

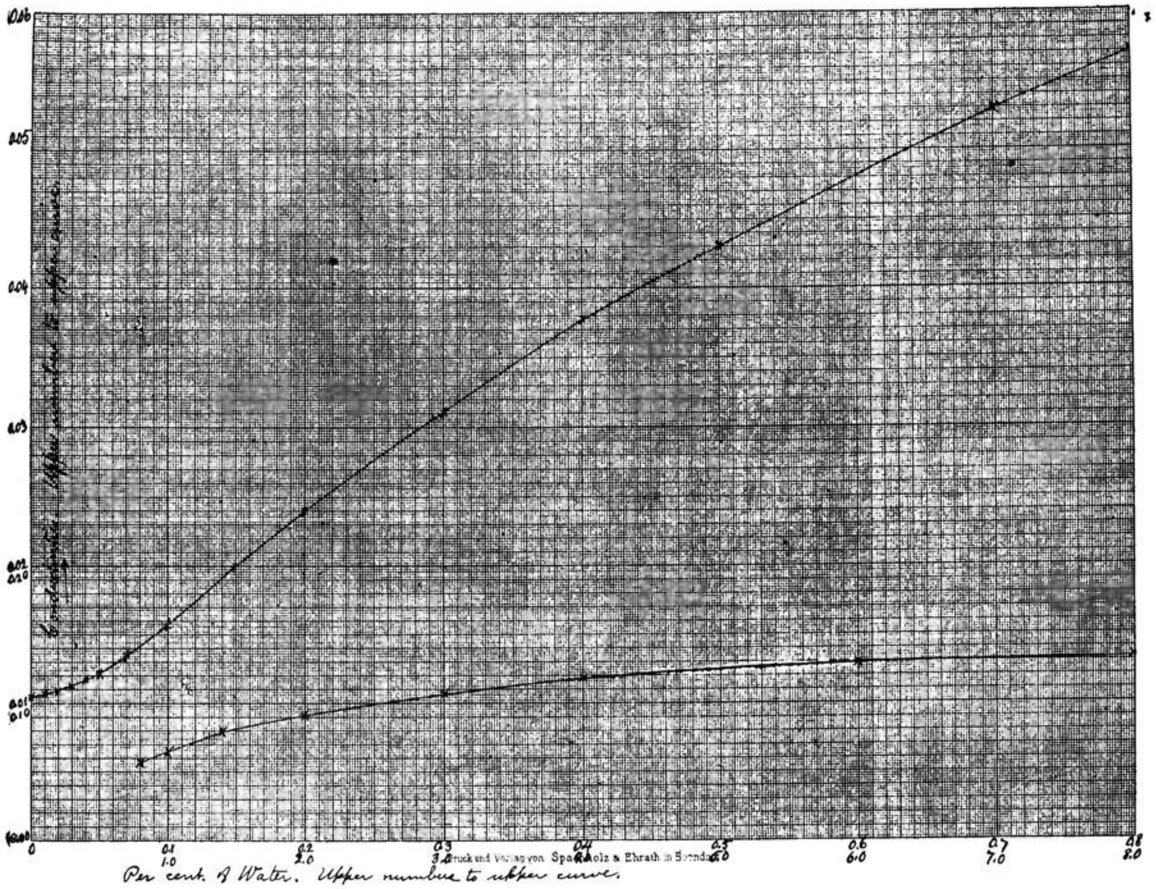

Plate I.

If the specific conductivity of sulphuric acid is 0.1250 reciprocal ohms or less, *i. e.*, contains 95 or a higher per cent. of acid, then the accuracy of analysis by means of the conductivity, for the most part, materially exceeds that of either the gravimetric or the volumetric analysis. This applies only to pure acid. The conductivity of a solution of 0.96 per cent. of potassium sulphate in absolute sulphuric acid, for instance, is 0.02469, about two-fifths of that of an acid containing the same percentage of water, or about the same as that of an acid containing 0.2 per cent. of water. The conductivity of sulphuric acid accordingly seems to be much less affected by a given percentage of a salt than by the same percentage of water.

TABLE II.

Per cent. of water.	Successive increments.	Diff.	Successive increments distributed.	Diff.	Idealized conductivities.
0.00	..	....	..	....	0.01041
	26		25		
0.01		—8		+4	0.01066
	18		29		
0.02		+31		+5	0.01095
	49		34		
0.03		—16		+7	0.01129
	33		41		
0.04		+11		+9	0.01170
	44		50		
0.05		+26		+11	0.01220
	70		61		
0.07		+2		+13	0.01342
	72		74		
0.10		+14		+13	0.01564
	86		87		
0.15		—6		—6	0.01997
	80		81		
0.20		—9		—9	0.02402
	71		72		
0.30		—4		—9	0.03121
	66		63		
0.40		—12		—8	0.03754
	53		55		
0.50		—4		—8	0.04302
	49		47		
0.70		—11		—8	0.05247*
	38		39		
1.00		—8		—8	0.06419
	30		31		
1.5		—8		—8	0.07963*
	22		23		
2.0		—6		—7	0.09110*
	16		16		
3.0		—5		—6	0.1071
	11		10		
4.0		—5		—4	0.1175
	6		6		
6.0		—4		—4	0.1292
	2		2		
8.0	..	....	..	....	0.1329
10.0	..	....	..	....	0.1299

It is interesting to note, that the maximum change in the conductivity of concentrated sulphuric acid, as shown in Table II, occurs at a concentration of about 99.85 per cent.

The exact location of the maximum conductivity reached by concentrated sulphuric acid has not been determined by this research, but seems to lie near 92 per cent. Knietsch found it at 92.01 per cent. The nearest measurements on each side of this concentration were made at 89.92 per cent. and 94.0 per cent.

Summary.

1. By this investigation, there has been worked out a method for obtaining pure, permanently low melting (unpolymerized) sulphur trioxide in relatively large quantities.

2. Absolute sulphuric acid was prepared by the direct interaction of its pure anhydride and water, brought together in stoichiometrical proportions.

3. It was found that the absolute sulphuric acid possesses a sharply defined minimum electrical conductivity and a sharply defined maximum

freezing point, both of which results confirm views held or conclusions arrived at by others.

4. It has then been proved that the preparation of absolute sulphuric acid may rightly be based on the minimum specific electrical conductivity or on the maximum freezing point.

5. It has been shown that for the analysis of 95 per cent. or more concentrated sulphuric acid, the electrical conductivity yields results whose error never seriously exceeds 0.01 per cent., and is generally less.

6. There has been arranged a table of specific electrical conductivities of sulphuric acid which may be used for analytical purposes.

Further work on the conductivity and other physical properties of sulphuric acid is now in progress. It is also hoped that sulphur trioxide may be more fully investigated both as to physical and chemical properties.

UNIVERSITY OF MICHIGAN, ANN ARBOR,
September, 1908.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS;[1] ALUMINICO-TUNGSTATES AND ALUMINICO-PHOSPHOTUNGSTATES.

BY LLOYD C. DANIELS.

Received August 31, 1908.

Some years ago Balke and Smith[2] described an ammonium and a silver ammonium aluminico-tungstate, $3(NH_4)_2O.Al_2O_3.9WO_3.4H_2O$ and $11Ag_2O.21(NH_4)_2O.4Al_2O_3.36WO_3$, in which the ratio of aluminum oxide to tungstic trioxide was 1 : 9. It seemed well to prepare other salts to learn whether this ratio was preserved in a series of such derivatives.

It was also desired to isolate the free aluminico-tungstic acid. A solution of it was, indeed, obtained, but upon evaporation, even at room temperature, decomposition occurred. When the solution was neutralized with ammonium hydroxide, a salt identical with that from which the acid was liberated, reappeared.

Aluminico-tungstic acid reacted acid to methyl orange, and in the cold displaced carbon dioxide from solutions of sodium bicarbonate. It is soluble in 50 per cent. or stronger alcohol, but on standing in such a solution the tungstic acid, or part of it, is reduced, a blue solution, but no precipitation, resulting. This acid was prepared by the method employed by Wolcott Gibbs and later workers, in liberating free complex inorganic acids; *i. e.*, by treating the mercurous salt with a little less than the amount of hydrochloric acid required to precipitate all of the mercury

---

[1] From the author's thesis for the Ph.D degree.

[2] THIS JOURNAL, 25, 1229.