339. *Solutions in Sulphuric Acid. Part XXII.*[*] *A Reinvestigation of the Electrical Conductivity of the Water–Sulphur Trioxide System, with Special Reference to the Composition of Minimum Conductivity.*

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The electrical conductivity of the water–sulphur trioxide system in the region of the composition H_2SO_4 has been reinvestigated. The values of the minimum conductivity and the composition at which it occurs have been determined at 10°, 25°, and 40° from experiments in which the electrical conductivity and the freezing point of the same solution in a combined conductivity cell and cryoscope were measured over a range of compositions in the neighbourhood of the composition H_2SO_4. New values are given for the conductivities of solutions of water and sulphur trioxide in sulphuric acid.

IN a previous investigation [1] of the electrical conductivity of the water–sulphur trioxide system in the neighbourhood of the composition H_2SO_4 it was found that at 25° the minimum conductivity occurs at the composition H_2SO_4 to within ± 0.003m (H_2O or $H_2S_2O_7$). At the freezing point of sulphuric acid (10·37°), Kunzler and Giauque [2] found that the minimum conductivity did not occur exactly at the composition H_2SO_4 but at 99·996 $\pm$ 0·001 weight % (*i.e.*, 0·002 $\pm$ 0·0005 mole of H_2O per kg. of solution). It was subsequently stated by Kunzler [3] that the composition of minimum conductivity changes by less than 0·003 weight % (*i.e.*, 0·0015 mole per kg. of solution) over the range 5—20°. It will be shown in a later paper that the exact position of minimum conductivity is of considerable importance in connection with the determination of the mobilities of the $H_3SO_4^+$ and HSO_4^- ions in sulphuric acid, and a knowledge of these mobilities is essential for an understanding of the mechanism of chain-conductance in sulphuric acid. Since neither Kunzler and Giauque [2] nor Kunzler [3] made any measurements at 25°, or gave actual conductivity values † at any temperature, we considered it worth while to repeat our earlier measurements at 25° with greater accuracy and to extend them to other temperatures. In order to achieve the accuracy necessary for this work and other work on the conductivities of solutions in sulphuric acid (see, *e.g.*, refs. 27 and 28), the conductivity bridge and cells used previously [1] were replaced by apparatus of considerably improved design.

EXPERIMENTAL

Conductance Bridge.—This consisted of an A.C. Wheatstone bridge network with a resistance-capacitance Wagner earth, the design being based on Luder's [4] precision bridge circuit. The resistance boxes used as standards were non-inductive 5-decade boxes (Doran Instrument Co. and Croydon Precision Instrument Co.) reading to 11,111 ohms in 0·1 ohm steps. They were calibrated by the method of self-comparison with an accuracy of 0·02%. For most measurements the bridge was supplied with 1000 c./sec. A.C. of pure sinusoidal-waveform at an input voltage of 0·8—1·0 v r.m.s. For tests of electrode polarisation a multi-frequency oscillator giving 300 to 10,000 c./sec. was used. The out-of-balance voltage from the bridge was fed into a two-stage audio-frequency amplifier [4] and was detected in sensitive headphones. With this apparatus and the use of the " separate terminal balance " method [4] a sharp balance point to 0·1 ohm in more than 10,000 ohms could be obtained.

Thermostats.—For an accuracy of 0·01% in the measurement of the resistance of sulphuric acid, which has a temperature coefficient [2] of approximately 4% per °c the temperature must be controlled to better than $\pm 0.003°$. The thermostats used were lagged copper tanks, each

* Part XXI, preceding paper.
† These authors measured the variation of the resistance of sulphuric acid with change of composition in a cell of unknown cell constant.

[1] Gillespie and Wasif, *J.*, 1953, 204.
[2] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 804.
[3] Kunzler, *Analyt. Chem.*, 1953, **25**, 93.
[4] Luder, *J. Amer. Chem. Soc.*, 1940, **62**, 89.

holding 15 gallons of Shell " Diala-B " transformer oil and equipped with an efficient stirrer and a mercury–toluene regulator. The temperatures were set by comparison with thermometers calibrated by the National Physical Laboratory. The absolute accuracy of their calibrations was $\pm 0.005°$, corresponding to an error of 0.02% in the absolute values of specific conductance. For the 25° tank the temperature was controlled by a T41 gas-filled triode and mercury–toluene regulator and remained constant to within $\pm 0.002°$. The thermostats at 10° and 40° were regulated within $\pm 0.01°$ by " Sunvic " hot-wire vacuum switches. The 10° tank was also fitted with a commercial refrigerator unit.
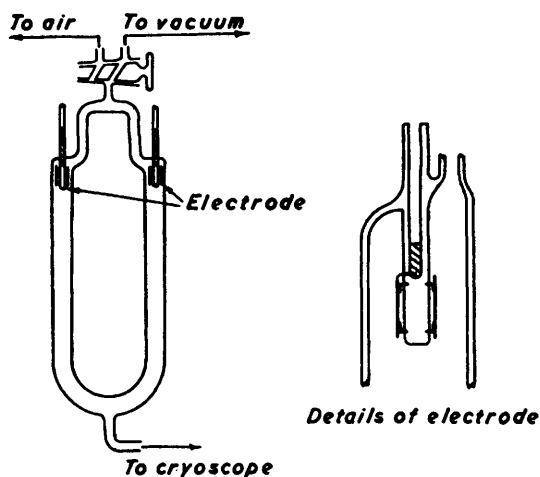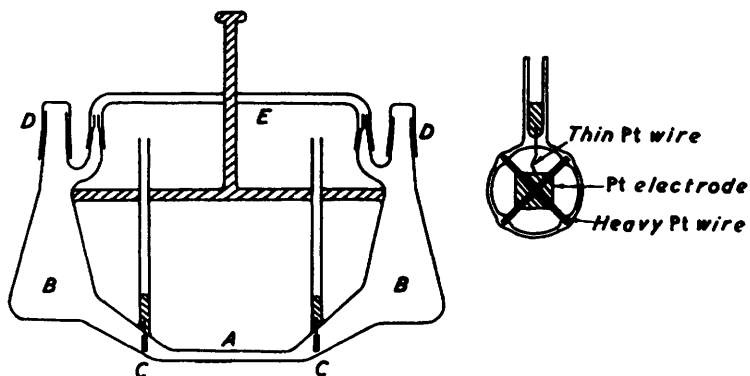

Fig. 1. *Conductivity cell I.*

Fig. 2. *Conductivity cell II.*

Conductivity Cells.—These were of " Pyrex " glass with pinch-sealed platinum electrodes. Some of the earlier measurements were made with the cells used previously by Gillespie and Wasif.[1] The electrode chamber of this type of cell was filled by a pressure of dry air. Most of the measurements were, however, carried out in cells of a new design which avoids the use of air pressure. In these cells (Fig. 1) the electrode chamber (A) joins the two flasks (B) which act as a reservoir, and it is therefore washed out each time the solution is poured from one flask to the other by tilting the cell. The solution is easily mixed after the addition of solute by repeatedly running the solution from one flask to the other by tilting. The electrodes (C) were attached rigidly to the sides of the cell by stout platinum wires as shown in Fig. 1. The mixing of the cell contents is facilitated when the cell is tilted because of the turbulent motion set up around the electrodes.

For experiments in which the freezing point and the conductivity of the same sample of solution were measured a combined cryoscope–conductivity cell was used. The conductivity

cell (Fig. 2) was U-shaped and communicated with the cryoscope [5] at its lower end. It was attached close to the side of the cryoscope. The size and shape of this cell were largely dictated by the necessity of being able to insert the whole combined cell into a suitable air-jacket for the freezing-point measurements. The cell was filled from the cryoscope, which acts as a reservoir, by means of suction applied through the two-way tap.

Great care was taken in the construction of the cells to eliminate all pinholes in the glass. In agreement with the earlier findings by Trenner and Taylor,[6] and contrary to the practice of some other workers,[7] conditioning of the electrodes, by electrodeposition of platinum black, was found to be necessary to eliminate electrode polarisation resistances. The platinising solution used was that recommended by Jones and Bollinger.[8] New electrodes were plated, " greyed " by heating to redness, and replated. The cells were then washed with distilled water, steamed for an hour, and dried in an oven at 120°. The cells were calibrated by means of Jones and Bradshaw's 0·1 D standard potassium chloride solution.[9] The potassium chloride was an " AnalaR " sample recrystallised three times from " conductance " water, then dried in an air-oven, and finally fused in a platinum dish. The " conductance " water was laboratory distilled water further purified by passing it through an ion-exchange column. It had a specific conductance of 1—2 × 10^{-6} ohm^{-1} cm.$^{-1}$. The calibrations were reproducible to better than 0·05%, although slightly greater changes in the cell constants of some of the cells were noticed over a period of a year or more, necessitating periodic recalibration.

Sulphuric Acid.—Commercial 65% oleum was refluxed for 10 hr. with chromium trioxide to decompose any oxidisable impurities, and then sulphur trioxide was distilled off at atmospheric pressure by gently heating, and condensed as the liquid at room temperature. This was twice redistilled and then distilled slowly into 98% " AnalaR " sulphuric acid, to form a concentrated oleum which was diluted as required by the addition of water or 98% " AnalaR " acid. All the samples of acid whose freezing points were measured had maximum freezing points above 10·361° in good agreement with the value of 10·365 ± 0·005° given by Gillespie and Oubridge.[10]

Procedure.—For the combined conductivity–freezing point experiments, a dilute oleum was weighed into the cell shown in Fig. 2, which was then placed in the 25° thermostat with continuous stirring of its contents until it had attained thermal equilibrium (about ½ hr.). By applying a slight pressure with dry air the electrode chamber was filled and then emptied again. The solution in the cryoscope was mixed by operating the reciprocating stirrer and the electrode chamber was refilled. This process was repeated several times to ensure thorough mixing of the solution. Ten to fifteen minutes after the final mixing the resistance of the cell was measured, then the mixing process and resistance measurement were repeated to ensure that the mixing and the washing of the electrode chamber had been complete. Finally, the cell was removed from the thermostat and the freezing point of its contents was measured, a platinum resistance thermometer and Smith's difference bridge being used.[5] Successive small weighed amounts of water were then added, the resistance and freezing point of the acid being measured after each addition. The concentration of the initial oleum was not known at the start of the experiment, but was calculated from the weight of oleum used and a plot of the freezing point against weight of water added, the maximum of which occurs at the composition H_2SO_4.

In experiments in which water was added the heat of reaction vaporised some of the water which then condensed on, or was absorbed by, a layer of acid on the glass walls of the cell out of contact with the liquid. The " lost " water was slowly absorbed by the surface layer of acid in the cell, with the result that a small change of conductivity took place each time the cell was shaken. Because of such drifts, the experiments in which water was added were rather tedious, the solutions often taking several hours to become homogeneous after each addition. Therefore, most experiments were carried out by adding water as a dilute solution in sulphuric acid, when, as the heat of solution was much smaller, no appreciable amount of water was vaporised and no drifts were observed. As the exact concentration of the aqueous acid added in these experiments was not known at the start of the experiment, a plot of the conductivities and concentrations obtained from the experiments in which water was added was used to determine the compositions of two solutions in the aqueous acid experiments. From a knowledge of the

[5] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.
[6] Trenner and Taylor, *J. Phys. Chem.*, 1931, **35**, 1336.
[7] *E.g.*, Brand, Horning, and Thornley, *J.*, 1952, 1374.
[8] Jones and Bollinger, *J. Amer. Chem. Soc.*, 1935, **57**, 280.
[9] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.
[10] Gillespie and Oubridge, *J.*, 1956, 80.

amount of aqueous acid added between these two compositions the concentration of the water in the aqueous acid was found, and the compositions of the other solutions were then calculated.

Once the conductivity of 100% sulphuric acid had been determined from experiments in which both the conductivity and the freezing point were measured, further experiments were carried out in which only conductivity was measured in cells of the type shown in Fig. 1. The compositions of the solutions were calculated as above from the initial weight of oleum taken and the weights of water or aqueous acid added, the conductivity of 100% acid being used instead of the maximum freezing point as the reference point.

The effect of temperature on the conductivity of the water–sulphur trioxide system was studied in experiments in which the composition was varied by the addition of aqueous acid. The conductivity of each solution was determined at 9·66°, 25°, and 40°, and its composition was found from the plot of the conductivity at 25° against composition obtained from previous experiments.

Results.

For purposes of discussion and comparison the results of conductivity measurements are generally most conveniently expressed in volume concentration units such as molarity or normality. Our solutions could not be made up with sufficient accuracy by volume and they were all made up by weight. In order to express the concentrations of the solutions in volume concentration units it is necessary to know their densities, but in the case of sulphuric acid solutions these are in many cases not known, or are not known with sufficient accuracy. We have found that it is generally most convenient to express our concentrations as moles of solute per kg. of solution (moles kg.$_{soln.}^{-1}$). This unit is not widely used and has no special name or symbol, although these would be useful, but it appears to have several advantages. Concentrations in molar units are simply obtained from concentrations in moles kg.$_{soln.}^{-1}$ units by multiplying the latter by the density of the solution. Many workers have attempted to avoid the difficulty caused by the lack of knowledge of densities of solutions by using instead the density of the solvent to give an approximate or " pseudo " molarity, but since they are often not careful to distinguish between this quantity and the true molarity, confusion is liable to arise. Mole-fractions and molalities suffer from the disadvantage that they can have more than one value in cases, for example, where the solute is dissociated, reacts with, or is solvated by, the solvent. Thus one can calculate a stoicheiometric molality on the assumption that the solute dissolves unchanged, or various " true " molalities depending on the particular assumptions made concerning the internal state of the system. Volume concentration units such as molarities do not have this disadvantage, but they are, on the other hand, temperature dependent, and have the disadvantage that a given molecular concentration has a different molarity at different temperatures. Concentrations expressed in mole kg.$_{soln.}^{-1}$ units are, however, independent of any assumptions concerning the internal state of the system, and they are also independent of temperature. Concentrations of oleums (*i.e.*, solutions of sulphur trioxide in sulphuric acid) are expressed in terms of disulphuric acid $H_2S_2O_7$ as this is the predominant species in the dilute oleums with which we are concerned.

It is not possible to give in detail the results of all the very large number of measurements that were made. The results of our measurements over the concentration range 0·015 mole of $H_2S_2O_7$ kg.$_{soln.}^{-1}$ to 0·015 mole of H_2O kg$_{soln.}^{-1}$ are shown in Fig. 3. The freezing points agree very well with the previous work of Kunzler and Giauque [2] and they serve to determine the position of the composition H_2SO_4 to better than 0·0005 mole kg.$_{soln.}^{-1}$. It can be seen that the minimum conductivity occurs on the aqueous side of the composition H_2SO_4. From a large-scale version of this plot it was concluded that the minimum value of the specific conductance at 25° of (1·0432 ± 0·0005) × 10^{-2} ohm^{-1} cm.$^{-1}$ occurs at a concentration of 0·0019 ± 0·0005 mole kg.$_{soln.}^{-1}$, and that at the composition H_2SO_4 the specific conductance is (1·0439 ± 0·0005) × 10^{-2} ohm^{-1} cm.$^{-1}$ (Table 3). The results of the conductivity measurements at 25° over the concentration range 0·15 mole of $H_2S_2O_7$ kg.$_{soln.}^{-1}$ to 0·1 mole of H_2O kg.$_{soln.}^{-1}$ are shown in Fig. 4. From large-scale versions of the plots shown in Figs. 3 and 4, and others covering a wider concentration range, values of the specific conductance at round concentrations were interpolated. These are given in Tables 1 and 2. Interpolated values obtained from the measurements made at 9·66° and 40·00° are also given in Table 1. The values at 9·66° and at 40·00° of the composition of minimum conductivity and the specific conductances at these compositions and at the composition H_2SO_4 are given in Table 3. The accuracy of the results

FIG. 3. *Freezing points and conductances in the region of the composition* H_2SO_4.
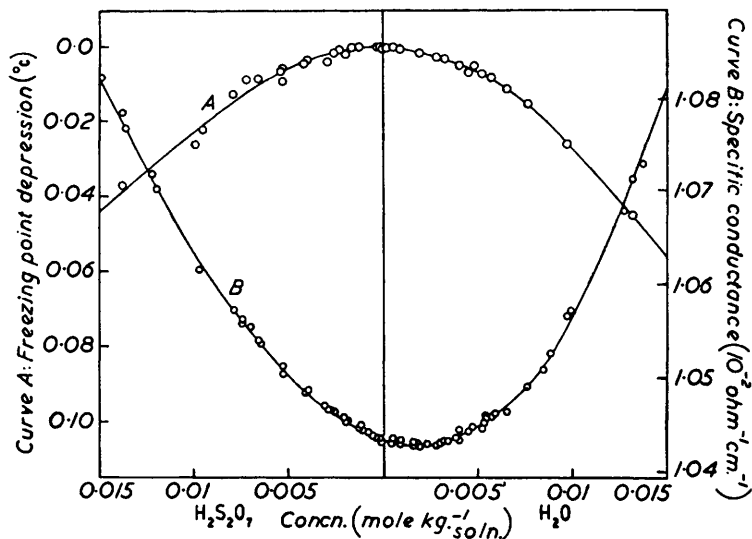
Curve A : Freezing-point depression (°c).   Curve B : Specific conductance (10^{-2} ohm^{-1} cm.$^{-1}$).

FIG. 4. *Specific conductance of dilute solutions of* H_2O *and* $H_2S_2O_7$ *in sulphuric acid.*
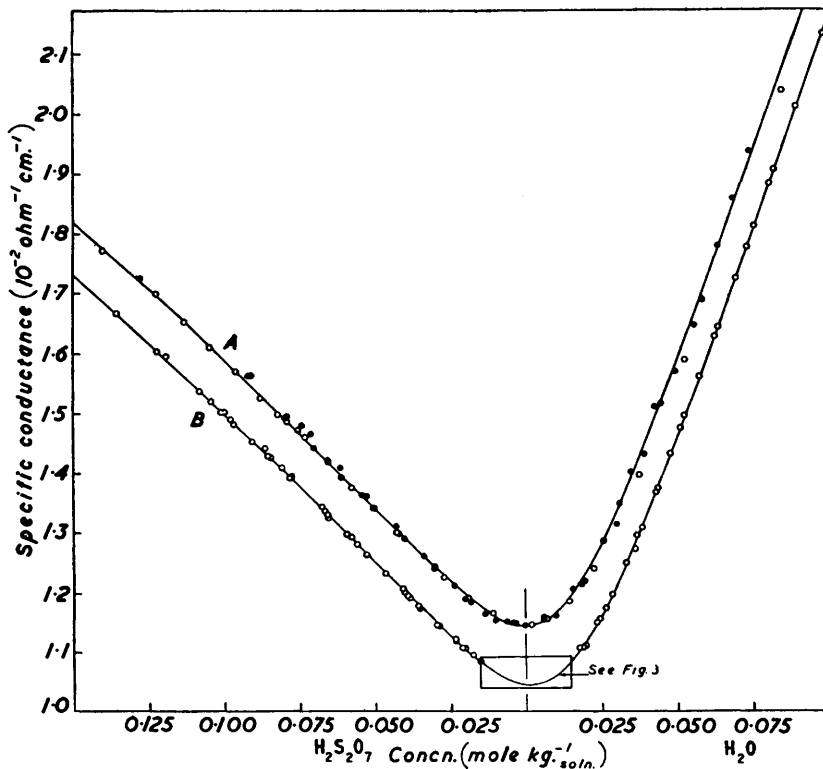
A {
  ○ Hetherington, Hub, Nichols, and Robinson (see ref. 24).
  ● Gillespie and Wasif.
  —— Mean curve of present work shifted vertically by 0·1 (10^{-2} ohm^{-1} cm.$^{-1}$) and horizontally to
       the left by 0·0019 (mole kg.$_{soln.}$$^{-1}$).

B {
  ○ Experimental points. } Present work.
  —— Mean curve.

at these temperatures is not as great as at 25° because of the fewer measurements made and because the temperatures of the thermostats were less accurately controlled.

TABLE 1. *Interpolated specific conductances* (10^{-2} *ohm*$^{-1}$ *cm.*$^{-1}$) *at low concentration at* 9·66°, 25·00°, *and* 40·00°.

Concn. (mole kg.$_{soln.}^{-1}$)	H$_2$S$_2$O$_7$			H$_2$O		
	9·66°	25·00°	40·00°	9·66°	25·00°	40·00°
0·000	0·5700	1·0439	1·7106	0·5700	1·0439	1·7106
0·001	0·5713	1·0447	1·7111	0·5690	1·0436	1·7103
0·002	0·5730	1·0459	1·7117	0·5685	1·0432	1·7103
0·003	0·5751	1·0473	1·7125	0·5686	1·0437	1·7105
0·004	0·5772	1·0489	1·7140	0·5691	1·0440	1·7109
0·005	0·5794	1·0506	1·715	0·5699	1·0453	1·712
0·006	0·5819	1·0530	1·717	0·5711	1·0467	1·713
0·007	0·5845	1·0554	1·718	0·5725	1·0483	1·715
0·008	0·5870	1·0579	1·722	0·5741	1·0505	1·717
0·009	0·5896	1·0608	1·724	0·5759	1·0533	1·719
0·010	0·5921	1·0639	1·727	0·5783	1·0570	1·723
0·012	0·5975	1·0709	1·734	0·5845	1·0658	1·731
0·014	0·6028	1·0783	1·742	0·5931	1·0761	1·742
0·016	0·6081	1·0861	1·750	0·6035	1·0876	1·756
0·018	0·6135	1·0942	1·759	0·6164	1·0994	1·774
0·020	0·619	1·102	1·769	0·632	1·112	1·793
0·030	0·652	1·148	1·821	0·717	1·208	—
0·040	0·687	1·199	1·878	—	1·327	—
0·050	0·727	1·251	1·940	—	1·453	—

TABLE 2. *Interpolated specific conductances* (10^{-2} *ohm*$^{-1}$ *cm.*$^{-1}$) *at higher concentrations at* 25·00°.

Concn. (mole kg.$_{soln.}^{-1}$)	H$_2$S$_2$O$_7$	H$_2$O	Concn. (mole kg.$_{soln.}^{-1}$)	H$_2$S$_2$O$_7$	H$_2$O	Concn. (mole kg.$_{soln.}^{-1}$)	H$_2$S$_2$O$_7$	H$_2$O	Concn. (mole kg.$_{soln.}^{-1}$)	H$_2$S$_2$O$_7$	H$_2$O
0·00	1·044	1·044	0·07	1·351	1·733	0·18	1·844	3·180	0·32	2·32	4·64
0·01	1·064	1·057	0·08	1·400	1·875	0·20	1·918	3·419	0·34	2·39	4·82
0·02	1·102	1·112	0·09	1·448	2·017	0·22	1·99	3·64	0·36	2·45	4·99
0·03	1·148	1·208	0·10	1·496	2·160	0·24	2·06	3·86	0·38	2·51	5·15
0·04	1·199	1·327	0·12	1·593	2·430	0·26	2·13	4·07	0·40	2·58	5·30
0·05	1·251	1·453	0·14	1·682	2·689	0·28	2·19	4·27	0·42	—	5·46
0·06	1·303	1·592	0·16	1·766	2·940	0·30	2·26	4·46	0·44	—	5·60

TABLE 3. *Specific conductances at the composition* H$_2$SO$_4$ *and at the composition of minimum conductance.*

Temp.	κ (10^{-2} ohm^{-1} cm.$^{-1}$) H$_2$SO$_4$	κ (10^{-2} ohm^{-1} cm.$^{-1}$) " Minimum "	Composition of minimum conductance (moles of H$_2$O kg.$_{soln.}^{-1}$)
9·66°	0·5700 ± 0·001	0·5685 ± 0·001	0·0023 ± 0·001
25·00	1·0439 ± 0·0005	1·0432 ± 0·0005	0·0019 ± 0·0005
40·00	1·711 ± 0·001	1·710 ± 0·001	0·0015 ± 0·001

DISCUSSION

The Specific Conductances of 100% *and Minimum-conductivity Sulphuric Acid.*—There have been a large number of determinations of either the conductivity of 100% H$_2$SO$_4$ or the minimum conductivity of the H$_2$O–SO$_3$ system,[7, 11-26] The apparatus and techniques

[11] Gillespie and Wasif, *J.*, 1953, 221.
[12] Walden, *Z. anorg. Chem.*, 1902, **29**, 371.
[13] Hantzsch, *Z. phys. Chem.*, 1907, **61**, 257.
[14] Lichty, *J. Phys. Chem.*, 1907, **11**, 225; *J. Amer. Chem. Soc.*, 1908, **30**, 1834.
[15] Bergius, *Z. phys. Chem.*, 1910, **72**, 338.
[16] Poma, *J. Chim. phys.*, 1912, **10**, 187.
[17] Kendall, Adler, and Davidson, *J. Amer. Chem. Soc.*, 1921, **43**, 1846.
[18] Hall and Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 237.
[19] Ussanowitsch, Samarakowa, and Udwenko, *Acta Physicochim. U.R.S.S.*, 1939, **11**, 505; *J. Gen. Chem. (U.S.S.R.)*, 1939, **9**, 1969.

used in earlier investigations were in general too insensitive and inaccurate to detect the very small differences of composition and of specific conductance between the acid of minimum conductivity and acid of composition H_2SO_4. The values obtained by Lichty,[14] Trenner and Taylor,[6] Brun,[21] Tutundzic and Liler,[23] and Hetherington et al.,[24] although less accurate, agree reasonably well with our own values.

The value of the minimum conductivity given by Gillespie and Wasif [11] is appreciably lower that that now obtained. There appear to be two main reasons for this. First, a redetermination of the cell constants of the cells used in the earlier work has shown that the original values were in error by almost 0·5%. Secondly, re-examination of the large-scale plots of the results obtained at 25° by Gillespie and Wasif suggests that they were in error in selecting a value of 0·01033 ohm^{-1} cm.$^{-1}$ for the minimum conductivity, even though a value as low as this was obtained in an individual experiment, and that a value of 0·01040 ohm^{-1} cm.$^{-1}$ would have been more consistent with their results. If these two corrections are made, their corrected value of 0·01045 ohm^{-1} cm.$^{-1}$ agrees reasonably well with the present work.

In calculating the uncertainty in our own value of $(1·0439 \pm 0·0005) \times 10^{-2}$ ohm^{-1} cm.$^{-1}$ for the specific conductance of 100% sulphuric acid, allowance has been made for the probable effect on the conductivity of small amounts of impurities known to be present in the " AnalaR " acid. In some experiments we measured the conductivity of acid that was known to be impure. Thus, one sample of acid which had become contaminated during storage and was slightly brown gave a reproducible minimum conductivity of 0·01034 ohm^{-1} cm.$^{-1}$—nearly 1% lower than the correct value. It is incorrect to assume that the lower the value of the minimum conductivity the purer the acid, not only because of this result but also because it has been shown that non-electrolytes in general cause a decrease in the conductivity of sulphuric acid.[11] For more accurate work it would be necessary further to reduce the amounts of the impurities in the sulphuric acid, in particular, as has been pointed out by Kunzler and Giauque,[2] of the dissolved air which is soluble to the extent of approximately 0·002 wt. %, and probably causes a slight decrease in the conductivity. It may be seen that our results on the composition of minimum conductance are in agreement with, and extend to other temperatures, those of Kunzler and Giauque.[2] Our determination of the specific conductance of " minimum conductivity " and 100% acid at 9·66°, 25°, and 40° provides values of greater accuracy than hitherto available, and shows that there is a very small difference between the values of these two quantities at each of the temperatures investigated. By assuming that Kunzler and Giauque's 100% acid had the same conductivity as ours at the temperature at which we made our measurements, we were able, by using their temperature coefficient, to calculate a value for their cell constant, and hence obtain conductivity values for their other solutions. Our results agree well with the values thus calculated and we have used these additional values to obtain the minimum conductivity at 9·66° more accurately than would have been possible from our results alone.

Conductivities of Solutions of Water and Sulphur Trioxide in Sulphuric Acid.—Earlier work on the conductivities of solutions of water and sulphur trioxide in sulphuric acid has been discussed by Gillespie and Wasif [11] and compared with their own results. Only Lichty's results [14] for water agreed well with their values.

The results obtained by Gillespie and Wasif and the recent work of Hetherington et al.[24] are compared with our own results in Fig. 4. The values obtained by Gillespie and Wasif have been corrected to take account of the errors in their cell constants as mentioned above.

[20] Reinhardt, *J. Amer. Chem. Soc.*, 1950, **72**, 3359.
[21] Brun, *Univ. i. Bergen Arbok*, 1952, *Naturvitenskap. Rekke*, 1953, No. 12, 1.
[22] Schwab, Zentelis, and Kassapoglu, *Chem. Ber.*, 1952, **85**, 508.
[23] Tutundzic and Liler, *Bull. Soc. chim., Belgrade*, 1953, **18**, 521.
[24] Hetherington, Hub, Nichols, and Robinson, *J.*, 1955, 3300.
[25] Tartakowskaya, Bondarenko, and Emelyanova, *Acta Physicochim. U.R.S.S.*, 1937, **6**, 609.
[26] Ussanowitsch and Tartakowskaya, *J. Gen. Chem. (U.S.S.R.)*, 1946, **16**, 1987.

The upper curve A in this figure is the mean curve obtained from our results, and the experimental points are due to Gillespie and Wasif and to Hetherington *et al.* This curve is identical with B except that it has been shifted vertically by $0 \cdot 1$ ohm^{-1} cm.$^{-1}$ and to the left, *i.e.*, towards the oleum side, by $0 \cdot 0019$ mole kg.$_{soln.}^{-1}$ so that its minimum occurs at the composition H_2SO_4 since in both these previous investigations it was assumed that the minimum conductivity occurs at this composition. It may be seen that there is generally quite good agreement between these experimental points and our mean curve although the scatter of the points is rather greater than in the present work, and the values of Hetherington *et al.* for solutions of water are somewhat lower than our present values.

Values of the specific conductance of solutions of water and disulphuric acid interpolated from our results are given in Tables 1 and 2. It is believed that they are more accurate than any previous values. They provide a very convenient and a very accurate means of determining the composition of dilute solutions of water or sulphur trioxide in sulphuric acid. They have been used in this way in several recent investigations.[27, 28]

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[27] Flowers, Gillespie, and Wasif, *J.*, 1956, 607.
[28] Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.