43. *Solutions in Sulphuric Acid. Part IX.* The Electrical Conductivity of the Water–Sulphur Trioxide System in the Region of the Composition of Sulphuric Acid.*

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The electrical conductivity of the water–sulphur trioxide system for compositions in the neighbourhood of sulphuric acid has been re-investigated at 25°. A few measurements have also been made at 10·4°. The results are discussed and compared with those of earlier investigations.

The work described in this and the following three papers represents a continuation of a detailed investigation of solutions in sulphuric acid, the first part of which was carried out by the cryoscopic method (Parts I—VIII; *J.*, 1950, 2473—2537 and 2997).

The conductivity of the water–sulphur trioxide system in the region of the composition of sulphuric acid was first investigated by Kohlrausch (*Wied. Ann.*, 1882, **17**, 69), who found a minimum conductivity at a composition of 99·75% of H_2SO_4 and 0·25% of H_2O at 25°. Later Knietsch (*Ber.*, 1901, **34**, 4107) found a minimum conductivity at 99·9% of H_2SO_4 and 0·1% of H_2O at 25°. Hantzsch (*Z. physikal. Chem.*, 1907, **61**, 257) was the first to make a systematic study by means of both conductivity and cryoscopic measurements of water, sulphur trioxide, and other solutes in sulphuric acid and he found a minimum conductivity of 0·0098 ohm^{-1} $cm.^{-1}$ at the composition 100% of H_2SO_4 at 25°. Further measurements were reported by Lichty (*J. Amer. Chem. Soc.*, 1908, **30**, 1834), who found a minimum conductivity of 0·01041 ohm^{-1} $cm.^{-1}$ at the composition of sulphuric acid at 25°. Bergius (*Z. physikal. Chem.*, 1910, **72**, 338) repeated and extended Hantzsch's work and found a minimum conductivity of 0·0097 ohm^{-1} $cm.^{-1}$ at the same composition and temperature. More recently Ussanowitsch, Sumarakowa, and Udowenko (*Acta Phys. Chim. U.R.S.S.*, 1939, **11**, 505) reported values of 0·0106 ohm^{-1} $cm.^{-1}$ at 25° and 0·0058 ohm^{-1} $cm.^{-1}$ at 10° for the conductivity of pure sulphuric acid. Reinhardt (*J. Amer. Chem. Soc.*, 1950, **72**, 3359) investigated the conductivity of solutions of sulphur trioxide and gave a value of 0·0108 ohm^{-1} $cm.^{-1}$ for the conductivity of the pure acid. In a very recent paper (*ibid.*, 1952, **74**, 804) Kunzler and Giauque have shown that the minimum conductivity at 10·37° occurs at 99·996 ± 0·001 wt. % sulphuric acid, but they did not give any specific conductivity values.

A detailed re-investigation of the electrical conductivity of the water–sulphur trioxide system at 25° in the neighbourhood of the composition of sulphuric acid is now reported. A few measurements have also been made at 10·4°.

Experimental

Conductivity Apparatus.—The Pyrex-glass cells used (Fig. 1) were a modified form of that originally designed by Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1411). The flask *A* was of about 500 cm.³ capacity. The electrode chamber *C* was 1 cm. in diameter and 20 cm. long and contained at each end a platinum electrode *D*, approximately 0·5 cm. in diameter. The electrode chamber was designed to give a measured resistance of greater than 1000 ohms, to minimise the Parker effect, and to provide good thermal contact with the thermostat liquid. The function of the flask *A* and the three-way tap *E* was to facilitate the study of a series of different concentrations of solutions of the same solute. The electrodes were freshly platinised before each experiment. The cell constants were determined by using potassium chloride solutions of known concentration. Values of the specific conductivities of these solutions were interpolated from a curve based on Jones and Bradshaw's data (*J. Amer. Chem. Soc.*, 1933, **55**, 1780).

A small cell (Fig. 2) was also used in certain experiments in which the freezing points of the solutions were also measured. Its cell constant was determined in the manner described above.

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* Part VIII, *J.*, 1950, 2997. The former serial title "Cryoscopic Measurements in Sulphuric Acid" has now been widened.

The bridge circuit was of conventional design and included a calibrated non-inductive dial resistance box, a non-inductive ratio-box, a balancing condenser across the resistance box and a simple Wagner earth. A.C. of 1000 cycles cm.$^{-1}$ was provided by a fixed-frequency Muirhead oscillator. The balance point was detected by means of a single-stage amplifier and head phones.

Materials.—Dilute oleum solutions were prepared by distilling sulphur trioxide from 60% oleum into 98% " AnalaR " sulphuric acid under reduced pressure at room temperature. " AnalaR " potassium chloride was recrystallised twice from conductivity water, and dried at 600° for 4 hours. Conductivity water was prepared freshly for each experiment in an all-glass (Pyrex) apparatus by distilling the laboratory distilled water from potassium permanganate and sodium hydroxide.

FIG. 1. *Conductivity cell.*

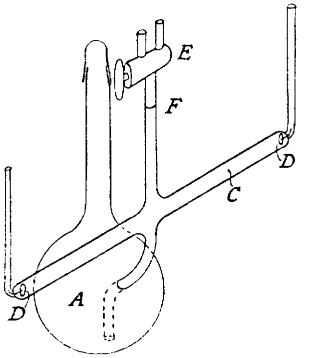
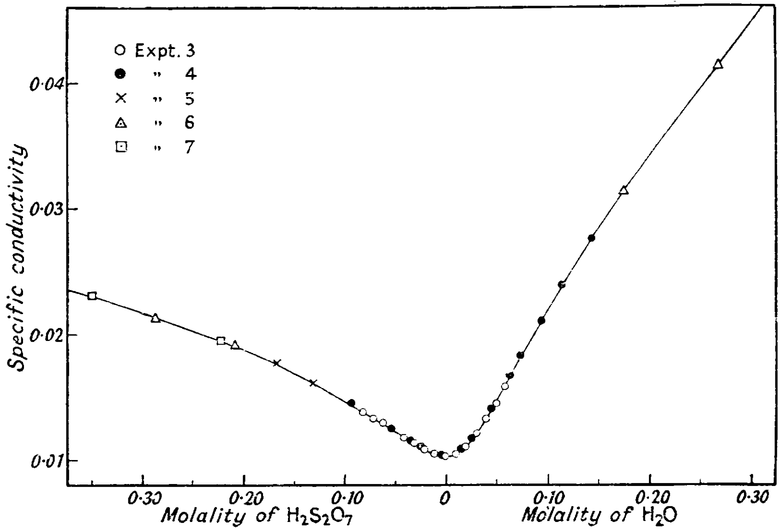


FIG. 2. *Conductivity cell for small amounts of solution.*

FIG. 3. *Specific conductivities of the system water–sulphur trioxide at compositions near that of sulphuric acid.*



Method.—Measurements were made in an oil-filled thermostat kept at 25·00° ± 0·01°. A few measurements were made at 10·4°. The cell was weighed empty, the flask *A* was filled with a dilute oleum, and the cell weighed again. The electrode chamber was then filled by applying suction through the three-way tap *E*. This solution was allowed to run back into the flask, the flask well shaken, and another portion sucked up. The electrode chamber was always washed several times in this manner before being finally filled to a mark on the tube *F*. During the whole operation the solution in the cell was protected from atmospheric moisture by phosphoric oxide guard-tubes. The conductivity was measured after the cell had been in the thermostat for ¾ hour. The electrode chamber was then emptied, the flask shaken, the electrode chamber refilled, and the conductivity measurement repeated in order to ensure that the solution had reached thermostat temperature and that the washing of the electrode chamber had been complete. Successive small weighed amounts of water were then added and the conductivity measured each time in the manner described above. The precise amount of sulphur trioxide in the initial acid was not known at the commencement of each experiment, but after all the conductivity measurements had been made all the concentrations could be calculated with the aid of the assumption that the composition at the minimum is that of sulphuric acid.

A number of experiments were also carried out in which the freezing point as well as the conductivity was measured for each composition. Freezing points were measured in the apparatus and by the method described in Part I (*loc. cit.*), and the conductivities were measured in the small cell shown in Fig. 2. Solutions were prepared in the cryoscope, the freezing point measured, and a sample then transferred to the conductivity cell and its conductivity measured.

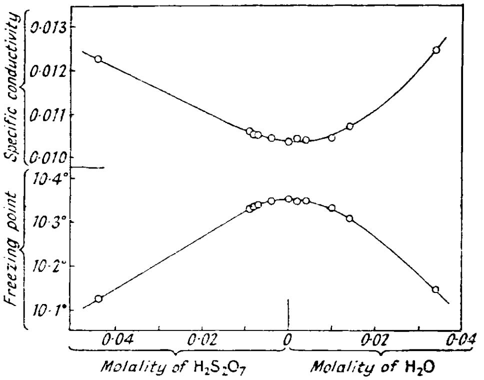


FIG. 4. *Comparison of specific conductivities and freezing points in the region of the freezing-point maximum.*

Results.—The results of the measurement of the specific conductivity (κ) of the water–sulphur trioxide system at 25° are given in Table 1. The results for low concentrations of water and sulphur trioxide are also shown graphically in Fig. 3. On the aqueous side of the composition of sulphuric acid, concentrations are expressed as molalities of water, but on the sulphur trioxide side they are given, not as molalities of sulphur trioxide, but as molalities of disulphuric acid, the assumption having been made that the solute sulphur trioxide is converted almost completely in dilute solutions into disulphuric acid (cf. Part II, *J.*, 1950, 2493).

TABLE 1. *The conductivity of the water–sulphur trioxide system at compositions near that of sulphuric acid at 25°.*

Expt. no.	Molality $H_2S_2O_7$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	Expt. no.	Molality $H_2S_2O_7$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	Expt. no.	Molality $H_2S_2O_7$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
7	1·5630	3·477	7	0·1043	1·493	3	0·0404	1·184
,,	1·1520	3·309	5	0·0935	1·454	4	0·0335	1·154
,,	0·9944	3·205	6	0·0803	1·387	6	0·0301	1·132
,,	0·8101	3·040	5	0·0752	1·370	4	0·0237	1·109
,,	0·6195	2·826	3	0·0710	1·335	5	0·0216	1·092
,,	0·4671	2·554	5	0·0661	1·315	6	0·0182	1·077
,,	0·3496	2·303	3	0·0617	1·286	4	0·0134	1·067
6	0·2863	2·127	5	0·0571	1·275	3	0·0110	1·047
7	0·2227	1·950	3	0·0509	1·234	6	0·0062	1·044
6	0·2075	1·903	4	0·0431	1·205	4	0·0032	1·041
5	0·1670	1·767	4	0·0401	1·205	—	0·0000	1·033
,,	0·1298	1·616						
Expt. no.	Molality H_2O	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	Expt. no.	Molality H_2O	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	Expt. no.	Molality H_2O	$10^2\kappa$ ohm^{-1} cm.$^{-1}$
6	0·7859	7·591	4	0·1149	2·385	4	0·0275	1·196
,,	0·6659	6·993	,,	0·0946	2·105	,,	0·0257	1·181
,,	0·5603	6·381	,,	0·0740	1·832	3	0·0197	1·114
,,	0·4541	5·676	,,	0·0635	1·673	4	0·0153	1·098
,,	0·3607	4·960	,,	0·0535	1·540	3	0·0100	1·053
,,	0·2675	4·133	,,	0·0445	1·409	4	0·0068	1·051
,,	0·1746	3·128	3	0·0392	1·326	6	0·0060	1·048
4	0·1442	2·758	3	0·0300	1·208	,,	0·0000	1·033

The results of the few measurements made at 10·4° are given in Table 2.

TABLE 2. *The conductivity of the water–sulphur trioxide system at compositions near that of sulphuric acid at* 10·4°.

Molality of $H_2S_2O_7$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	Molality of $H_2S_2O_7$	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	Molality of H_2O	$10^2\kappa$, ohm^{-1} cm.$^{-1}$	Molality of H_2O	$10^2\kappa$, ohm^{-1} cm.$^{-1}$
0·0516	0·740	0·0072	0·587	0·0064	0·599	0·0678	1·139
0·0367	0·684	0·0000	0·580	0·0200	0·681	0·0990	1·447
0·0218	0·625			0·0363	0·826	0·1472	1·882

In order to determine the exact composition at which the conductivity minimum occurs, some experiments were carried out in which the freezing point as well as the conductivity at 25° was measured for each composition. The data obtained in these experiments are shown in Fig. 4.

It can be readily seen that, to within the accuracy of our measurements, the conductivity minimum at 25° occurs at the same composition as the freezing-point maximum, *i.e.*, at the composition of sulphuric acid. It certainly cannot differ from this composition by more than 0·003 mole kg.$^{-1}$. The value of the specific conductivity at the minimum in the conductivity curve, which is also therefore the conductivity of sulphuric acid, was found from the present results to be 0·01033 ohm^{-1} cm.$^{-1}$ at 25° and 0·00580 ohm^{-1} cm.$^{-1}$ at 10·4°.

DISCUSSION

Our value of the specific conductivity of sulphuric acid at 25° is compared with that of previous investigators in Table 3. Although our value is not as low as those of Hantzsch (*loc. cit.*) and Bergius (*loc. cit.*), it seems reasonable to suppose that our acid was pure, since it was prepared in the manner described in Part I and had a maximum freezing point of 10·36°, which was the highest freezing point we could obtain. Gable, Betz, and Maron recently (*J. Amer. Chem. Soc.*, 1950, **72**, 1445) obtained a value of 10·37°. That our specific conductivity value is probably reliable is emphasised by the fact that it was obtained numerous times in two independently calibrated cells.

TABLE 3. *The specific conductivity of sulphuric acid at* 25° (κ in ohm^{-1} cm.$^{-1}$).

Hantzsch (1907)	0·0098	Ussanowitsch *et al.* (1939)	0·0106
Lichty (1908)	0·01041	Reinhardt (1950)	0·0108
Bergius (1910)	0·0097	This investigation (1952)	0·01033

Hantzsch's values (*loc. cit.*) cannot in any case be regarded as very reliable, for the conductivity cells they used were not particularly suitable for such a highly conducting liquid as sulphuric acid, and their measured resistances were consequently very small and hence not very accurate. Furthermore, the technique of making conductivity measurements has been considerably improved since Hantzsch's time. Lichty's value (*loc. cit.*) is in quite good agreement with ours, but the recent values of Ussanowitsch *et al.* (*loc. cit.*) and of Reinhardt (*loc. cit.*) are not. The reasons for these higher values are not clear, but Reinhardt's values of the conductivity of solutions of disulphuric acid are also in very poor agreement with ours and those of other workers, thus suggesting that his conductivity measurements are not reliable.

Sulphuric acid has a very large conductivity for a pure liquid, larger in fact than for any other liquid that has been investigated with the exception of nitric acid and fused salts. This may be attributed to its extensive self-dissociation, which has been shown by cryoscopic measurements (Parts I, II, and IV) to be partly an autoprotolysis $2H_2SO_4 = H_3SO_4^+ + HSO_4^-$ and partly a self-dehydration : $2H_2SO_4 = H_3O^+ + HS_2O_7^-$.

The disulphuric acid branch of the conductivity curve in Fig. 3 is less steep than the water branch, and this is in accord with the conclusion from cryoscopic measurements (Part II) that water is almost fully ionised according to the equation $H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$, whereas sulphur trioxide is very largely converted into disulphuric acid, which is only partly ionised according to the equation $H_2S_2O_7 + H_2SO_4 = H_3SO_4^+ + HS_2O_7^-$. The conductivities of these two solutes are further discussed in relation to other solutes in Part XII (*J.*, 1953, 221).

In Fig. 5 a selection of the results given in Table 2 have been replotted, the concentrations of water and disulphuric acid being expressed in molarities by use of the density data reported in Part XI (*J.*, 1953, 215), and compared with the results of previous investigators. It may be seen that our results for water agree quite well with those of Lichty (*loc. cit.*) over the whole concentration range investigated, while the specific conductivities obtained by Hantzsch (*loc. cit.*) and by Bergius (*loc. cit.*) are as much as 10% lower than our values at corresponding concentrations. Our results for disulphuric acid do not agree very well with those of any of the previous investigators. The agreement with the results of Bergius (*loc. cit.*) is fair, his specific conductivity values being approximately 5% lower than ours.

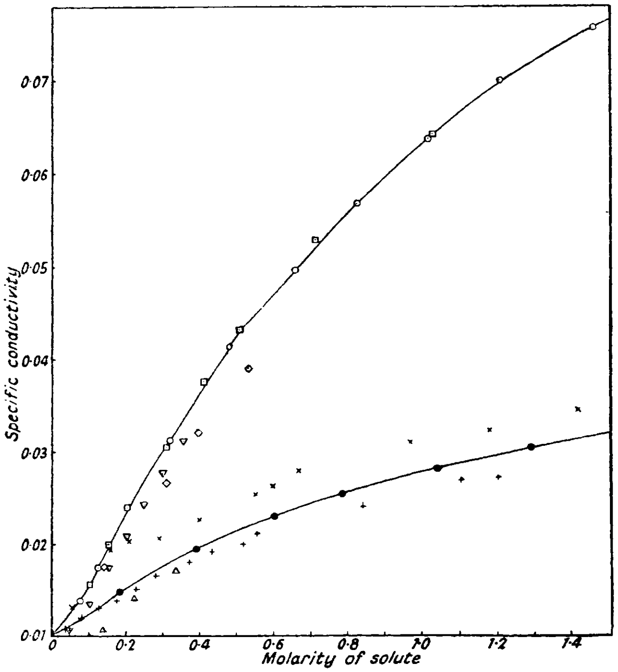


FIG. 5. *Comparison of the specific conductivities of water and disulphuric acid with the values obtained by earlier workers.*

H_2O:
- ○ *This investigation.*
- ⊡ *Lichty.*
- ▽ *Bergius.*
- ◇ *Hantzsch.*

$H_2S_2O_7$:
- ● *This investigation.*
- × *Reinhardt.*
- + *Bergius.*
- △ *Hantzsch.*

There is no agreement at all with Reinhardt's results (*loc. cit.*). Our results seem to be in agreement with those of Brand, Horning, and Thornley (*J.*, 1952, 1374) who, although they give no actual experimental results, state that the specific conductivities they obtained agreed best with those of Lichty (*loc. cit.*) for aqueous acids and those of Bergius (*loc. cit.*) for oleum.

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