either one-half or one centimeter apart and have vulcanite knobs upon which to rest the fingers. As soon as the approximate reading is found with one key the block is moved until both keys when pressed give a tone of the same intensity; the middle point is then the true minimum. It is well to have the one key movable so that the distance between the contacts may be reduced as the point is reached. By the use of this arrangement it is possible to find the point within a small fraction of a millimeter and much less experience is necessary for accurate results than by the ordinary process.

ON THE SURFACE-TENSIONS OF MIXTURES OF SULPHURIC ACID AND WATER, AND THE MOLECULAR MASS OF SULPHURIC ACID.

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THE apparatus employed in making the measurements of the surface-tension was that described in a previous number of this Journal.[1]

The sulphuric acid used was Baker and Adamson's "chemically pure" (sp. gr. 1.84), and was found on analysis to contain 4.98 per cent. of water. This acid was mixed in varying proportions with water and the mixtures analyzed. The specific gravities of some of the mixtures were determined, but most of them were taken from Lunge and Isler's tables[2] and the corrections for temperature applied by means of the data given by Bineau.[3]

The thermostat consisted of a beaker filled with water and provided with a stirrer. A layer of heavy oil was poured over the water so as to prevent evaporation. Readings were taken (never less than three at the same temperature) at intervals of about 5°. These were plotted and a smoothed curve (which was approximately a straight line) drawn through them. From this curve, readings were taken at temperature-intervals of 10°, and these were used in calculating the surface-tensions.

Readings were taken in the same way with pure water, from which with the aid of Ramsay and Shields' data[4] on the surface-

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[1] This Journal, **18**, 514 (1896).

[2] *Ztschr. angew. Chem.*, 129 (1890). Landolt and Börnstein, 196.

[3] *Ann. chim. phys.* (3), **26**, 123 (1849).

[4] *Ztschr. phys. Chem.*, **12**, 433 (1893).

tension of water at various temperatures, the values of the "apparatus constant" were calculated for every 10°. These were found to change slightly but regularly.

The numerical results of the determinations are given in the following table and are represented graphically in Figs. I and II. Curves for 0°, 20° and 50° only are drawn in Fig. I so as not to crowd too much. As it is, the right-hand parts of the curves practically coincide.

SURFACE-TENSIONS OF MIXTURES OF SULPHURIC ACID AND WATER.

2.65 per cent. H_2SO_4.

Temperature.	Apparatus constant.	Distance between ends of tubes in 0.025 inch.	Specific gravity.	Surface tension in dynes per cm.
0°	1.260	56.39	1.021	73.60
10°	1.266	55.71	1.019	72.69
20°	1.273	54.83	1.017	72.02
30°	1.278	54.04	1.015	71.13
40°	1.283	53.12	1.013	70.07
50°	1.290	52.13	1.011	69.01
		5.16 per cent. H_2SO_4.		
0°	1.260	55.83	1.037	74.02
10°	1.266	55.01	1.035	73.14
20°	1.273	54.18	1.033	72.31
30°	1.278	53.31	1.031	71.29
40°	1.283	52.43	1.029	70.43
50°	1.290	51.54	1.027	69.33
		11.87 per cent. H_2SO_4		
0°	1.260	54.02	1.081	74.75
10°	1.266	53.46	1.078	74.10
20°	1.273	52.86	1.075	73.48
30°	1.278	52.15	1.072	72.58
40°	1.283	51.32	1.069	71.52
50°	1.290	50.41	1.066	70.45
		18.33 per cent. H_2SO_4.		
0°	1.260	51.61	1.138	75.30
10°	1.266	51.00	1.133	74.44
20°	1.273	50.37	1.128	73.59
30°	1.278	49.72	1.125	72.75
40°	1.283	49.05	1.123	71.92
50°	1.290	48.30	1.118	70.90
60°	1.296	47.64	1.113	69.95
70°	1.303	46.87	1.108	68.89

35.13 per cent. H_2SO_4.

Temperature.	Apparatus constant.	Distance between ends of tubes in 0.025 inch.	Specific gravity.	Surface tension in dynes per cm.
0°	1.260	47.03	1.275	77.19
10°	1.266	46.75	1.268	76.68
20°	1.273	46.41	1.262	76.34
30°	1.278	46.05	1.255	75.45
40°	1.283	45.67	1.248	74.68
50°	1.290	45.26	1.242	74.05
60°	1.296	44.76	1.235	73.15
70°	1.303	44.22	1.228	72.25

58.05 per cent. H_2SO_4.

0°	1.260	40.03	1.494	77.60
10°	1.266	39.98	1.486	77.44
20°	1.273	39.95	1.478	77.25
30°	1.278	39.88	1.470	77.08
40°	1.283	39.78	1.462	76.76
50°	1.290	39.66	1.454	76.49
60°	1.296	39.46	1.446	76.03
70°	1.303	39.22	1.438	75.55

65.27 per cent. H_2SO_4.

0°	1.260	37.75	1.575	77.41
10°	1.266	37.74	1.567	77.34
20°	1.723	37.72	1.559	77.29
30°	1.278	37.70	1.531	77.13
40°	1.283	37.68	1.543	76.99
50°	1.290	37.65	1.535	76.89
60°	1.296	37.61	1.527	76.74
70°	1.303	37.40	1.519	76.31

80.45 per cent. H_2SO_4.

0°	1.260	28.84	1.752	66.60
10°	1.266	28.78	1.743	66.40
20°	1.273	28.65	1.734	66.32
30°	1.278	28.60	1.725	66.00
40°	1.283	28.56	1.716	65.92
50°	1.290	28.55	1.707	65.79
60°	1.296	28.50	1.698	65.67
70°	1.303	28.48	1.689	65.50

83.23 per cent. H_2SO_4.

0°	1.260	27.11	1.783	64.18
10°	1.266	27.09	1.774	64.09
20°	1.273	27.06	1.764	63.89

Temperature.	Apparatus constant.	Distance between ends of tubes in 0.025 inch.	Specific Gravity.	Surface tension in dynes per cm.
30°	1.278	27.02	1.755	63.70
40°	1.283	27.00	1.746	63.54
50°	1.290	26.99	1.737	63.48
60°	1.296	26.97	1.728	63.37
70°	1.303	26.96	1.718	63.19
95.02 per cent. H_2SO_4.				
0°	1.260	23.63	1.843	58.26
10°	1.266	23.54	1.833	57.97
20°	1.273	23.46	1.824	57.76
30°	1.278	23.40	1.814	57.53
40°	1.283	23.39	1.805	57.43
50°	1.290	23.36	1.796	57.36
60°	1.296	23.31	1.786	57.28
70°	1.303	23.24	1.775	56.89

The foregoing data show that both the addition of water to sulphuric acid and of sulphuric acid to water increases the surface-tension of the liquids. The increase in the surface-tension of the acid even when but a small proportion of water is mixed with it is especially marked. The maximum surface-tension is observed when about equal quantities of the two liquids are mixed. It is also shown that certain mixtures of sulphuric acid and water, although of different percentage composition, may yet have equal surface-tensions. This is clearly brought out in the curves for mixtures containing 58.05 per cent. and 65.27 per cent., respectively, of the acid; the curves cross at an abscissa-value of about 22°. Besides this observed instance, other mixtures have a similar behavior. The limits of the values of their composition and surface-tensions may be learned by an inspection of the figures.

A noteworthy peculiarity of strong solutions of sulphuric acid in water is the slight influence that changes of temperature have upon their surface-tensions. The curves in Fig. 2 become more and more horizontal the greater the percentage of acid in the mixtures. From these low values found for the temperature coefficients, certain conclusions may be drawn as to the degree of molecular polymerization of pure sulphuric acid. It is true that no determinations were made of the surface-tension of the pure acid, but it seems reasonable to conclude that the regularity of the curves would extend to the abcissa-value of the pure acid. Yet it is scarcely to be expected that anything like correct values for the surface-tension of the pure acid would be obtained by extrapolation, for the curves are too steep and close together. All that is legitimate to infer is that the pure acid has a small temperature coefficient with respect to its surface-tension.

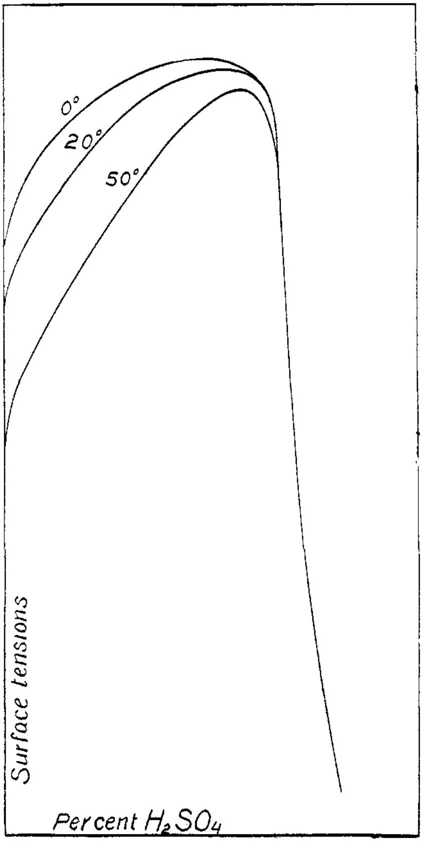

Fig. 1.

Now according to the views of Ramsay and Shields[1] the degree of polymerization of a liquid may be estimated by means of the change of its molecular surface energy with the temperature. The smaller this is, the greater is the degree of polymeri-

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[1] *Loc. cit.*

zation of a liquid's molecules. The small temperature coefficient of sulphuric acid points then to a high degree of polymerization; the molecular mass of its molecule must be several times 98, the molecular mass corresponding to the formula H_2SO_4. Ramsay in a lecture before the Chemical Society of Paris[1] stated that he had found it probable that the molecule of sulphuric acid could be approximately represented by the formula $(H_2SO_4)_{23}$. If this be true, sulphuric acid has the most complex molecule of any liquid as yet examined in that regard, and this complexity of

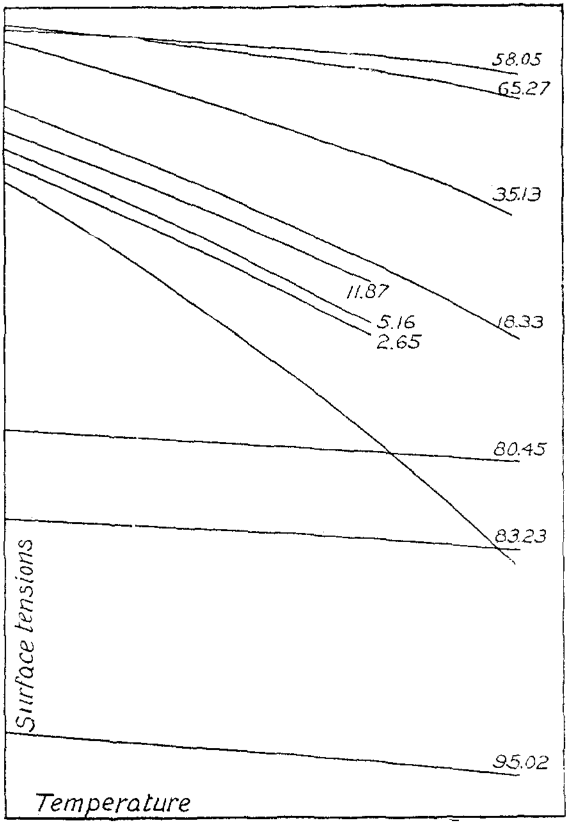

Fig. 2.

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[1] This was printed in the *Revue Scientifique* (4), 2. 1 (1894). No data or details seem to have been given in any of the journals devoted to the publication of chemical research.

molecular structure may account for many of the anomalous properties of mixtures of sulphuric acid and water.

The conclusion that sulphuric acid is molecularly polymerized to a very considerable extent would indicate in accordance with the views of Nernst[1] and Brühl[2] that the pure acid should have a large dielectric constant and high dissociative power. The specific inductive capacity of sulphuric acid has not been determined and no measurements of the electric conductivity of salts dissolved in it have been made. The electric conductivity of a concentrated acid may, indeed, be regarded as due to the ions of water, for the acid may be considered to be the solvent and water the dissolved substance. If the dielectric constant of pure sulphuric acid should be found to be larger than that of water, it seems in the light of the views of Nernst and Brühl quite natural to suppose that the acid would exert a not inconsiderable dissociative power on water. Still even in concentrated acid, the extraordinary dissociative power of water would assert itself, and the acid regarded as solvent would become dissociated into its ions in part. The circumstance that the acid may dissociate into more than two ions together with the probability that it is molecularly polymerized, complicates matters greatly.

The fact found by Kohlrausch[3] that a 10 per cent. solution of water in sulphuric acid presents a maximum of conductivity may perhaps be taken as an indication that the acid actually does assert a dissociative action on water; that the conductivity of stronger solutions of acid in water are quite small may be due to the great viscosity of the acid solvent. It would be premature, however, to enter more at length into discussions of this nature, because of the fewness of the data and because the work of Kahlenberg and Lincoln[4] shows that not so very much reliance can be placed on the views of Nernst and Brühl.

[1] *Ztschr. phys. Chem.*, **13**, 3 (1894).

[2] *Ibid.*, **18**, 514 (1895) and **27**, 317 (1898).

[3] Pogg. *Ann.*, **159**, 233 (1876).

[4] *J. Phys. Chem.*, **3**, 12 and 457 (1899).