164. *The Solubility of Sulphur Dioxide in Fuming Sulphuric Acid.*

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The solubilities of sulphur dioxide in fuming sulphuric acid have been determined at 20° in acid containing from 0 to 72% of free sulphur trioxide and at 40° and 60° in acid of concentration ranging from 80% H_2SO_4 to 20% free SO_3.   The solubility curves show evidence of the compounds H_2SO_4,H_2O and H_2SO_4,SO_3.   To obtain a rough check on the applicability of Henry's law, some measurements of the equilibrium absorption from a gas mixture containing 6% of sulphur dioxide were also made.

THE solubility of sulphur dioxide in fuming sulphuric acid is of general interest and has some technical importance. "Oleum" is produced by absorption of sulphur trioxide from an atmosphere which also contains the dioxide

and, in dependence on the temperature, the concentration of the absorbing sulphuric acid, and other conditions, more or less of this gas may remain dissolved in the final product.

On the solubility of sulphur dioxide in fuming acid no data have been published. For sulphuric acid in the range 55—98% H_2SO_4 the solubilities at 20° in g. % of solution were determined by Miles and Fenton (*J.*, 1920, **117**, 59). Corresponding values at 41° and 62° were given by Cupr (*Rec. Trav. chim.*, 1928, **47**, 55) (see Fig. 2). Lopatto and Sawinaeff (*J. Appl. Chem. U.S.S.R.*, 1934, **7**, 881) investigated the composition of the sulphur dioxide–sulphuric acid mixtures which were in equilibrium with sulphur dioxide–air mixtures containing up to 24%, and occasionally up to 38%, of the dioxide, at temperatures between 20° and 60°, but they worked only with sulphuric acid concentrations in the range 62—70%. In the work reported here, many determinations were made of the solubility of the dioxide in oleum of concentrations varying from 0 to 22% of pure sulphur trioxide (81·63—95% total SO_3), and others, not so numerous as those at 20°, were carried out at 40° and 60° in the lower range from 80% H_2SO_4 to 20% free SO_3 (65—85% total SO_3). In addition, since the solubilities of sulphur dioxide determined at atmospheric pressure in the absence of air cannot be used to calculate the amount dissolved at a lower pressure, or in a dilute dioxide–air mixture, unless the amount dissolved is proportional to the partial pressure, some measurements were made of the amount of sulphur

FIG. 1.
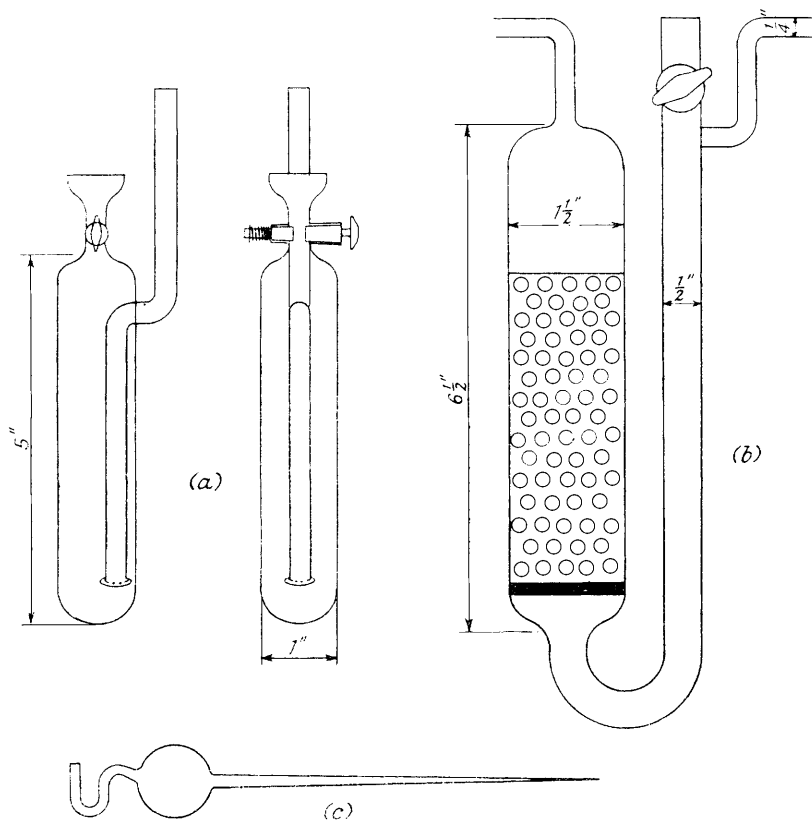
dioxide taken up by three varieties of acid (of 80, 96, and 104% H_2SO_4) from 6% mixtures of sulphur dioxide and air, in order to find out how far Henry's law could be relied on in this case.

The whole of the experimental data for 20°, 40°, and 60°, with the exception of a single result which was obviously in error, are given in Table I and in Figs. 2 and 3. The values given on the graphs and in the second columns of the table are stated in g. of dioxide dissolved in 100 g. of acid and have been corrected to correspond with an atmosphere of dioxide at 760 mm. pressure, by multiplying each of the experimental values by the factor $760/(P-p)$, in which P is the atmospheric pressure recorded during the process of saturation, and p is the vapour pressure of sulphur trioxide above the oleum at the temperature of saturation. The values of p were taken from previous work reported by McDavid (*J. Soc. Chem. Ind.*, 1924, **43**, 57T) and by Miles, Niblock, and Wilson (*Trans. Faraday Soc.*, 1940, **36**, 345). In Fig. 2 the black dots on the uppermost graph represent the results obtained by Miles and Fenton (*loc. cit.*) for sulphuric acid of 60—100% H_2SO_4 content at 20°. The results of the present work are plotted as circles on this graph and also in Fig. 3, in which the curve is shown extended into the region of higher trioxide concentration on a rather larger scale. Besides the well-known minimum of solubility corresponding very nearly to the dihydrate of sulphur trioxide (H_2SO_4,H_2O containing 84·5% H_2SO_4), there is a distinct inflexion of the curve, which appears to fall to a minimum very nearly at the point
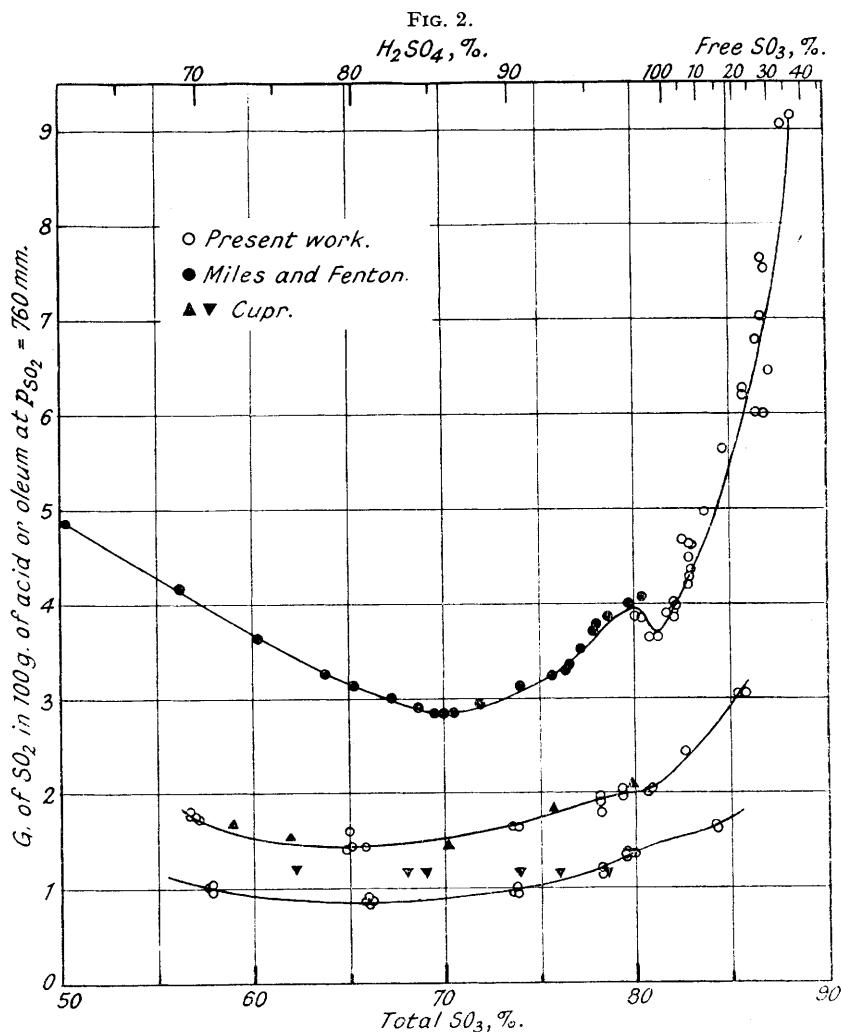
FIG. 2.

TABLE I.

Solubility of Sulphur Dioxide in Sulphuric Acid and Oleum.

% total SO_3 = 100 $SO_3/(SO_3 + H_2O)$; % SO_2 = g. of SO_2 dissolved by 100 g. of acid or oleum, corrected for a pressure of 760 mm. of SO_2.

Total SO₃, %.	SO₂, %.	Total SO₃, %.	SO₂, %.	Total SO₃, %.	SO₂, %.	Total SO₃, %.	SO₂, %.	Total SO₃, %.	SO₂, %.
				Temperature 20°.					
80·21	3·85	82·17	3·98	84·57	5·62	87·90	9·06	93·30	18·93
80·37	3·81	82·53	4·66	85·77	6·18	88·30	9·17	93·30	20·42
80·64	3·66	82·75	4·18	85·94	6·27	88·60	9·58	93·34	20·28
80·81	3·65	82·8	4·58	86·47	6·77	88·90	9·41	94·20	23·31
81·63	3·88	82·85	4·33	86·49	5·99	90·65	11·98	94·60	22·13
82·03	3·95	82·90	4·60	86·65	5·99	90·70	12·05	95·22	25·78
82·07	3·85	82·90	4·48	86·71	7·06	91·10	12·17	95·02	27·58
82·12	3·91	82·91	4·28	86·93	7·52	91·30	12·14	95·10	28·34
82·13	3·96	83·65	4·96	87·11	6·47	93·16	18·73	95·23	28·16
				Temperature 40°.					
56·75	1·798	64·99	1·602	73·70	1·634	79·39	2·035	85·0	3·176
56·90	1·747	65·04	1·406	78·15	1·920	79·52	2·050	85·0	3·132
56·90	1·764	65·13	1·431	78·20	1·792	80·80	2·020	—	—
57·0	1·712	65·87	1·406	78·20	1·928	80·95	2·050	—	—
57·05	1·702	73·64	1·628	79·38	1·981	82·70	2·468	—	—
				Temperature 60°.					
57·75	0·983	66·03	0·834	73·82	0·953	79·50	1·346	84·30	1·625
57·9	0·986	66·14	0·848	73·87	0·990	79·57	1·337	84·40	1·610
57·91	0·988	66·23	0·858	78·22	1·196	79·60	1·359	—	—
65·88	0·855	73·75	0·949	78·31	1·172	79·90	1·371	—	—

corresponding to the composition of the monohydrate (H_2SO_4). As trioxide is added to its monohydrate, the solubility of the dioxide rises very steeply. At about 50% of free trioxide, *i.e.*, at a point close to the composition of pyrosulphuric acid (free $SO_3 = 45\%$), there is evidence of another slight but unmistakable inflection.

The solubilities at 40° and 60° were measured over a narrower range—from 70% H_2SO_4 to 20% oleum—chosen to include most of the acids of technical importance. The two curves show the same general relation as before; the principal minimum is apparent, although at a lower SO_3/H_2O ratio, and there are distinct bends in the neighbourhood of the monohydrate. The points marked by triangles represent the results obtained by

FIG. 3.
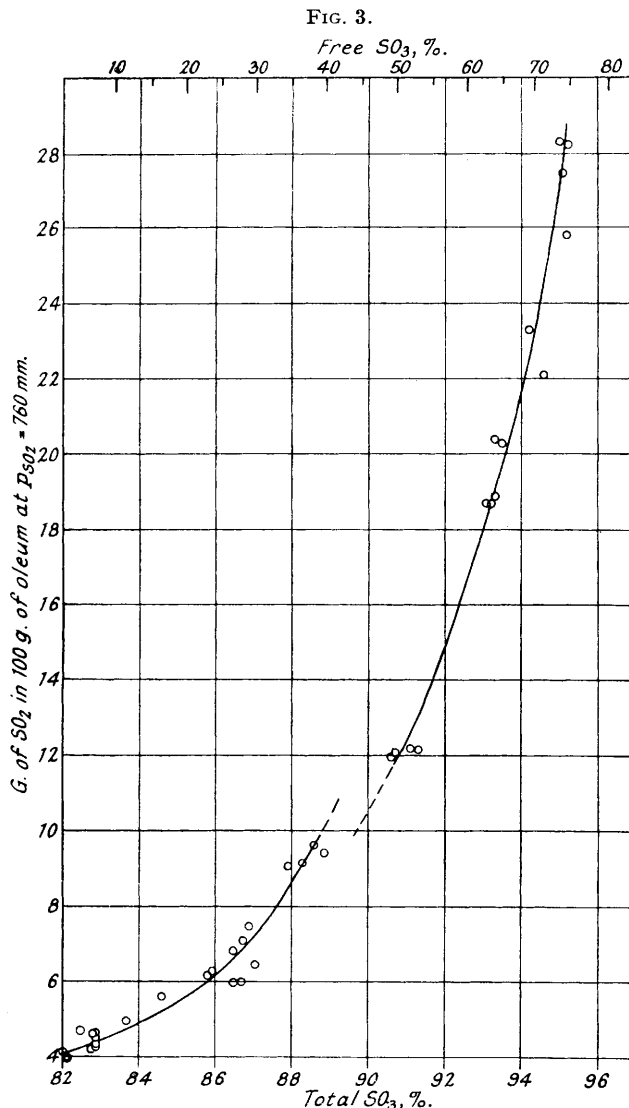
Cupr at 41° and 62°. A line drawn through his points at 60° would be straight and horizontal to an improbable degree.

The results of the determinations of the absorption of dioxide from mixtures of this gas and air are given in Table II. Only average results are stated, each being the mean of 3—6 determinations from separate experiments. Three concentrations of acid—80·2% H_2SO_4, 96·5% H_2SO_4, and an oleum containing 17·8% of free SO_3—were used. The gas mixture chosen was one of 6·0% of dioxide and 94% of air. The last column of each section of the table gives the ascertained weight of dioxide in 100 g. of acid, corrected to correspond to a pressure of 0·06 × 760 mm. of dioxide. The middle column of each section gives the calculated weight as 0·06S, S being the solubility, already stated in Table I, in g. of dioxide/100 g. of acid at 760 mm. pressure of the dioxide. The determined and calculated figures agree fairly well at 20°. At this temperature the assumption of Henry's law in calculating the absorption of the dioxide from any plant gas mixture would not lead to serious error, but at higher temperatures the calculated amounts of absorption are less than the experimental figures show, by an amount which is on the average about 10% at 40° and 15% at 60°.

<div align="center">TABLE II.</div>

Comparison of actual and calculated absorption of sulphur dioxide from a 6% gas mixture by sulphuric acid at 20°, 40°, and 60°.

	80.2% H$_2$SO$_4$; 65.4% total SO$_3$.			96.5% H$_2$SO$_4$; 78.6% total SO$_3$.			104.0% H$_2$SO$_4$; 17.8% free SO$_3$.		
Temp.	S, g./ 100 g. of acid.	0.06S.*	G. of SO$_2$/ 100 g. of acid (found).	S, g./ 100 g. of acid.	0.06S.*	G. of SO$_2$/ 100 g. of acid (found).	S, g./ 100 g. of acid.	0.06S.*	G. of SO$_2$/ 100 g. of acid (found).
20°	3.10	0.186 (−0.54%)	0.187	3.80	0.228 (+2.7%)	0.222	5.70	0.342 (0.0%)	0.342
40	1.43	0.086 (−11.7%)	0.0974	1.95	0.117 (−7.2%)	0.1260	2.90	0.174 (−9.9%)	0.193
60	0.85	0.051 (−20.0%)	0.0637	1.28	0.0768 (−11.0%)	0.0863	1.74	0.105 (−12.5%)	0.120

* Percentages show the difference between determined results and those calculated from the solubility of pure SO$_2$, as a proportion of the former.

<div align="center">EXPERIMENTAL.</div>

Apparatus and Method.—The absorber (Fig. 1a) was a glass vessel 5″ long and 1¼″ wide, closed by a large tap, the plug of which was secured by a spring. The cup above the tap was intended to make filling easier, but proved to be unnecessary. The gas-leading tube entered through the side, and its end was blown into a bulb perforated with a number of fine holes.

The acid or oleum was poured into the dry absorption tube through a funnel with a long thin stem, inserted through the bore of the stopcock, and was weighed in the tube. The thermostat in which the absorber was clamped was filled with clear transformer oil to minimise the effect of the oleum escaping if the vessel cracked or broke. Sulphur dioxide from a siphon was passed in through the inlet tube. To a branch tube between the siphon and the absorber was connected a pressure regulator which consisted of a U tube containing a little water, at the most enough to form a column in the tube 2″ high. The gas was passed at such a rate that streams of bubbles issued from the small holes of the inlet tube, and that a few bubbles came through the water in the U tube. When the air in the absorber had been displaced, the tap was turned off, and the vessel shaken vigorously for about 5 minutes. Then it was allowed to stand for 10 minutes, after which the shaking was repeated, the gas being able to enter freely through the inlet tube all the time. The tap of the absorber was not opened after the air had been displaced at the beginning; if it were, air was apt to enter, and to lower the sulphur dioxide content of the acid. After 1—2 hours no bubbles rose from the inlet tube when the vessel was shaken. Saturation was then complete.

Analysis.—Samples were taken for analysis in "oleum bulbs" (Fig. 1c) by inserting the capillary of a bulb through the open tap and sucking up about 2 g. of oleum. The capillary was sealed in a flame, and a rubber plug was inserted in the suction tube of the sampling bulb to prevent the escape of dioxide. After being weighed, the bulb was placed, capillary downwards, in a glass bottle containing either 25 or 50 c.c. of N/10-iodine solution and 300—400 c.c. of water, and the bulb was then broken by shaking. The closed bottle and its contents were allowed to stand until the fume had settled. When the stopper of the bottle was removed, the remains of the bulb were thoroughly broken with a glass rod. The excess of unreduced iodine was then titrated with N/10-thiosulphate solution in the usual way, and the total acidity was found by titrating with N-sodium hydroxide solution with methyl-red as indicator. From the result of this titration, to determine the acidity due to the sulphuric acid or sulphur trioxide present before any dioxide was added, an amount equivalent to twice the iodine added must be subtracted in accordance with the equation SO$_2$ + H$_2$O + I$_2$ = H$_2$SO$_4$ + 2HI.

This method of analysis was tested in several ways. (1) It was first shown that no trioxide was lost when bulbs filled with oleum were broken under water or under iodine solution. Estimations of the same oleum gave 83.33, 83.39% of SO$_3$ when the bulb was broken under water containing sodium hydroxide, 83.43, 83.45% under water alone, and 83.3% under water containing 25 c.c. of N/10-iodine solution. (2) The iodine titration is not affected by the presence of sulphuric acid. A solution of sodium metabisulphite was made, and measured volumes were titrated with iodine and thiosulphate with and without the amount of sulphuric acid to be expected : no difference could be found. (3) The sampling bulbs were found to lose weight during weighing in the customary way with oleum in them. This was overcome by sealing one end after the bulb had been filled, and putting a rubber stopper into the other. (4) Two samples were taken from the same oleum saturated with sulphur dioxide, one sample by suction, and the other by forcing the oleum into the bulb by applying an air pressure above the oleum in an earlier form of absorption vessel which allowed of this being done. The two samples gave the same result. Suction did not therefore reduce the dioxide content of the liquid.

When gas containing only 6% of sulphur dioxide was used, it was found much harder to reach equilibrium and a more efficient absorber was necessary. Fig. 1(b) is a diagram of it. The body contained glass beads supported on a loosely-fitting porous plate. The gas was passed in through the side tube. Just so much acid (about 60 c.c.) was used that the bubbling caused some of it to be carried up into the glass beads. The gas mixture was delivered from an apparatus used to mix sulphur dioxide and air for laboratory catalyst tests. Its dioxide content was within the limits 5·9—6·1%. To avoid the removal of sulphur trioxide from the oleum in the absorber, the gas mixture was passed first through Drechsel bottles containing about 250 c.c. of the same oleum, and standing in the same thermostat. Equilibrium was reached in 4 hours or more. Samples for analysis were drawn into oleum bulbs, the drawn-out stems of the bulb being inserted through the stopcocks as before.

It may be added that the technique of these measurements, of both solubility and of absorption from 6% mixtures, proved difficult, and that numerous determinations were necessary to give confidence in the results.

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