751. *The Vapour Pressure of the System Sulphuric Acid–Disulphuric Acid.*

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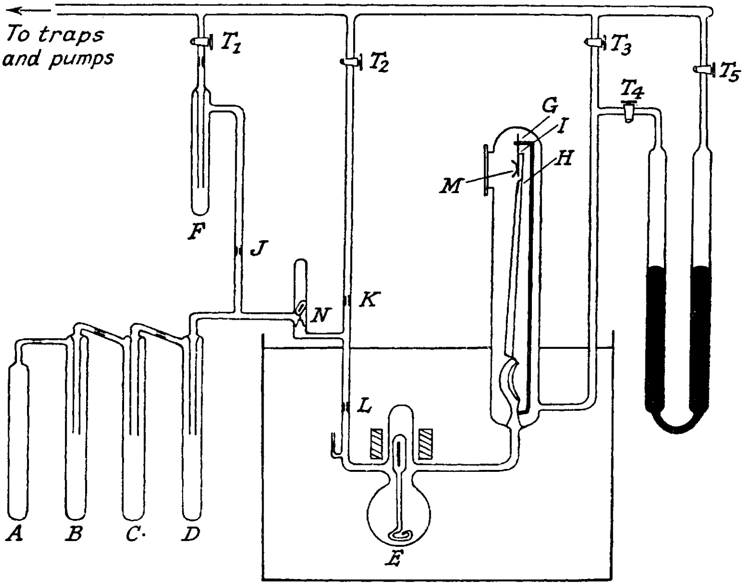
The vapour pressure of fuming sulphuric acid in the range of composition 50—63 moles % of sulphur trioxide (0—35% of " free " sulphur trioxide) has been determined at 20—80° by a static method. Where comparison is possible the measured pressures are usually lower than previously recorded values and reasons for this are discussed. The molar heat of evaporation of sulphur trioxide from the solution is in reasonably good agreement with thermal data. The measurements do not support the view that the oleums come into equilibrium slowly with respect to the components.

In the course of experiments on the mechanism of aromatic sulphonation in fuming sulphuric acid (*J.*, 1950, 997, 1004) an attempt was made to evaluate the relative activity of the $HO{\cdot}SO_2^+$ cation in different media from the activity of sulphur trioxide and the H_0 function of the acid. Several determinations of the vapour pressure of fuming sulphuric acid have been published, but only a limited number of measurements referred to the required range of temperature and composition and the agreement between different authors left much to be desired. Re-determination of the vapour pressure of dilute oleums and application to the kinetics of aromatic sulphonation are discussed in this and the following paper.

Vapour-density determinations prove that sulphur trioxide vapour is unimolecular. The pure solid and the liquid phase, however, are complex aggregates of uni- and multi-molecular forms of sulphur trioxide, and equilibrium between them is only established rapidly in the presence of traces of water. The anhydrous systems come into equilibrium very slowly and the physical properties show pronounced variations depending upon the history of the sample. Sulphur trioxide in dilute solution in sulphuric acid is present very largely as disulphuric acid, $H_2S_2O_7$ (this acid ionises slightly in the solution), but a small proportion exists in a free or physically solvated condition and is responsible for the vapour pressure. Apart from the low values of the vapour pressure, the conversion of the sulphur trioxide into disulphuric acid is demonstrated by Raman-spectral (Millen, *J.*, 1950, 2589) and freezing-point measurements (Gillespie, *J.*, 1950, 2493). It may be mentioned briefly that the vapour pressure is approximately proportional to the stoicheiometric molar ratio $H_2S_2O_7/H_2SO_4$ throughout a considerable range of composition, as shown (on a logarithmic scale) in Fig. 2B. Owing to the equilibrium $SO_3 + H_2SO_4 \rightleftharpoons H_2S_2O_7$, the pressure of sulphur trioxide is proportional to $([H_2S_2O_7]/[H_2SO_4]).f_{H_2S_2O_7}/f_{H_2SO_4}$, and it is, therefore, an experimental fact that this expression is very nearly proportional to the stoicheiometric ratio, moles $H_2S_2O_7/H_2SO_4$. This is readily understood if the equilibrium concentration of free sulphur trioxide, compared with that of disulphuric acid, is small.* On the question of whether the uncombined sulphur trioxide in the solution is unimolecular or associated, however, there is no direct evidence.

The present measurements relate to moderately dilute oleums in the range of composition 50—63 moles % of sulphur trioxide (0—35% by weight of "free" sulphur trioxide). Workers in this field have reported widely different results and no wholly definitive reason for this can be given. It has been suggested that the fuming acids do not come to equilibrium rapidly and that the properties depend upon the pre-treatment or the method of preparation, but it is difficult to accept this hypothesis because traces of water (*i.e.*, sulphuric acid or polysulphuric acids) are sufficient to establish equilibrium rapidly in pure liquid sulphur trioxide. The present measurements provide no evidence of "ageing" of the oleums, or of other effects of this kind.

FIG. 1.



EXPERIMENTAL

General.—The vapour pressure was measured by a static method, with a glass Bourdon gauge calibrated directly as a deflection instrument. The acid was prepared by distilling sulphur trioxide, purified by several preliminary fractionations, into sulphuric acid in a flask attached to the pressure gauge in an otherwise evacuated apparatus. Concentrated oleum (*ca.* 70% of "free" sulphur trioxide) seved as a convenient source of sulphur trioxide, and was prepared by distillation of sulphur trioxide from commercial oleum in a glass apparatus at atmospheric pressure. The oleum was pre-treated with chromium trioxide to remove sulphur dioxide.

The Bourdon Gauge.—The Pyrex-glass Bourdon gauge was required to measure accurately to 0·1 mm. and to withstand pressure differences of 100 mm. The movement of the pointer was magnified optically and mechanically : a mirror, *M* (Fig. 1), suspended on needle-points at *G*, was actuated by the movement of the pointer, *H*, attached to the gauge, and the deflection of the mirror was observed on a scale at 1·3 m. The sensitivity of the assembly was controlled by the distance I—G between the needle-points and the thrust of the pointer; in most cases 1 mm. of gas deflected the image on the scale by about 3 cm., and the apparatus was sensitive to pressure changes of 0·02 mm.

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* The analysis of sulphuric acid oleum is conveniently expressed in terms of the concentration of "free" sulphur trioxide, *i.e.*, sulphur trioxide present in excess of the composition H_2SO_4. In dilute oleums most of the sulphur trioxide under this heading is actually present as disulphuric acid, only a small concentration being genuinely free.

For measuring pressure up to 10 mm. the gauge was calibrated directly as a deflection instrument. Most of the recorded pressures fell in this range. At higher pressures air was admitted to the outside of the gauge, and in this case the vapour pressure was obtained as the sum of the external pressure, read on a conventional mercury manometer (15 mm. diam.), and the pressure difference across the gauge, represented by the residual deflection. The approximately linear pressure-deflection characteristic of the gauge was determined at 20° and 80° and was found to be independent of temperature. The null-point, which was slightly sensitive to temperature changes, was also determined at these temperatures and interpolated otherwise.

Preparation of Fuming Sulphuric Acid.—The apparatus is shown diagrammatically in Fig. 1. It was assembled for each run with concentrated oleum in the vessel *A* and " AnalaR " concentrated sulphuric acid in the pressure flask *E*. Dry air was used for the necessary glass-blowing. The contents of *A* were frozen to −80° and the apparatus evacuated by a two-stage mercury diffusion pump and a rotary pump. The accessible glass was heated with an oxygen flame, particularly at the constrictions used later for sealing. Without this treatment, sulphur trioxide tends to sublime on the walls of the apparatus and there is a possibility of decomposition during sealing-off.

Sulphur trioxide was distilled from *A* into *B*, and successively re-distilled into *C* and *D*. For this purpose the receiver was cooled to −80° and the distilling flask warmed gently. After each distillation the distilling flask was sealed off at a constriction and the distillate of sulphur trioxide pumped out through the tap T_1 for several hours, and finally the flask *D* was isolated from the manifold by sealing at *J*. Meanwhile the sulphuric acid in the flask *E* was degassed at 100° by pumping through T_2, and the constriction *K* was closed. To prepare the oleum, the breakable seal at *N* was opened and sulphur trioxide was distilled from *D* into *E*, the sulphuric acid in *E* being stirred and cooled in an ice-bath. Considerable pressures of sulphur trioxide developed during this distillation, which was carried out slowly to protect the guage. After distillation was complete, the contents of *E* were cooled to −80° and the constriction at *L* sealed. At this stage the null-point of the gauge was checked against earlier readings with the apparatus empty, but no measurable pressure of permanent gas was ever observed.

Throughout the distillations and the degassing the taps T_4 and T_5 were closed to prevent mercury vapour entering the system. T_1 was protected by a liquid-air trap *F* to avoid attack on the lubricant by sulphur trioxide vapour. After the pressure measurements the apparatus was opened, and the acid decanted and analysed (*J.*, 1946, 585). The gauge was found to return to its null-point when the pressures were equalised by admission of air.

Measurement of Vapour Pressure.—In general, pressures were taken at 10° intervals between 20° and 80°. During the measurements the flask and gauge were wholly immersed in a water-thermostat, controlled to ±0·05°, and the acid was stirred intermittently by an electromagnetically operated stirrer. The equilibrium value of the vapour pressure was reached in about 1 hour and was the same, within experimental error, whether approached from higher or lower temperature.

Expt. 23. Oleum, 26·7% of SO_3.

Temp. (° c)		10	20	30	40	50	60	70
Vapour pressure (mm.)	(*a*)	0·62	1·47	3·42	6·65	13·08	—	—
	(*b*)	—	1·47	3·43	6·63	13·10	25·67	49·20

(*a*), (*b*); equilibrium approached from higher and lower temp. respectively.

The system was tested for gauge errors by measuring the vapour pressure of water at 15—36°. In this experiment the gauge was sensitive to 0·1 mm. only, and the results were as follows :

Temp. (°c)	15·0	20·0	25·0	30·0	36·0
Vapour pressure (mm.)	12·8	17·6	23·7	31·9	44·6 (found)
	12·79	17·54	23·76	31·82	44·56 *

* From Landolt–Bornstein's " Tabellen."

Note on the Methods of Reading the Bourdon Gauge.—Tests showed that the gauge could be used equally well as a null or deflection instrument (Table 1). In measurements by Miles, Niblock, and Wilson (*Trans. Faraday Soc.*, 1940, **36**, 345), however, the external pressure was adjusted to bring the pointer of the gauge to an arbitrary " negative " reference mark, the pressure on the outside of the gauge being greater than the vapour pressure of the liquid under test. The compensating pressure was read on a manometer, and the vapour pressure of the liquid evaluated by subtracting the value of the external pressure required to bring the pointer to the reference mark with zero pressure inside the gauge. But the pressure needed to move the pointer from the null-point to the " negative " reference mark actually varies with the pressure inside the gauge, and the method gives high results (Table 1, compare lines 1 and 2 with line 3). The error is fairly small, but appreciable at low pressure.

TABLE 1. *Vapour pressure reading (mm.) with positive, zero, and negative deflections of the Bourdon gauge.*

Direct deflection	5·00	14·30	20·75	44·30	74·70
Null-point	4·95	14·30	20·70	44·30	74·70
" Negative " ref. mark	5·45	14·85	21·20	44·85	75·30

DISCUSSION

There are four comparatively recent series of measurements of the vapour pressure of mixtures of sulphuric acid and sulphur trioxide. The first is due to McDavid (*J. Soc. Chem. Ind.*, 1924, **43**, 57T) who investigated oleums containing up to 40% of " free " sulphur trioxide at 40—90° by a transpiration method. The second is published in the form of a table of smoothed values in the International Critical Tables (Vol. III, p. 304; cf. Gel'fmann, *Zhur. Priklad. Khim.*, 1948, **21**, 839), no indication of the method being given. The third and fourth series are measurements by static methods. Miles, Niblock, and Wilson (*loc. cit.*) investigated six oleums in the concentration range 6—65% of sulphur trioxide, for the most part at elevated temperatures so that pressures below 12 mm. were excluded from their discussion, and Remy and Meins (*Ber.*, 1942, **75**, 1901) measured the pressures of ten oleums in the range 11—98% of sulphur trioxide at 20—40°. Some pioneer determinations were also made by Knietsch (*Ber.*, 1901, **34**, 4111) but his values do not fit with any of the later measurements. None of the published results is in quantitative agreement, although the agreement between McDavid and Miles and his co-workers is fairly good. Otherwise the differences may be very large; occasionally they represent a *factor* of ten.

The results in this paper refer to 3—35% oleum at 20—80° (Table 2). This range of variables overlaps in part with all the earlier series, but the results do not agree well with any of them. The best agreement is with McDavid and, although only qualitative, it is still better than between any other independent pair of measurements. On the average

TABLE 2. *Partial pressure of sulphur trioxide in the system* H_2SO_4–$H_2S_2O_7$.

Composition, SO_3, moles %	51·1	51·5	51·5	52·9	53·1	54·3	56·0	57·9	59·4	60·8	61·0	61·7	62·5
" Free " SO_3, %	3·37	4·50	4·65	8·69	9·37	13·0	17·8	22·8	26·7	30·2	30·6	32·5	34·0
Temp.						Vapour pressure, mm.							
10°	—	—	—	—	—	—	—	0·49	0·62	—	—	—	—
20	—	—	—	—	—	0·55	0·81	1·19	1·47	2·18	2·40	3·70	5·40
25	—	—	—	—	—	0·75	—	—	—	—	—	5·15	—
30	—	—	—	0·63	0·70	0·98	1·48	2·27	3·43	4·62	5·10	7·25	7·95
35	—	—	—	—	—	1·31	—	—	—	—	—	10·1	—
40	0·52	0·52	0·54	1·10	1·25	1·77	2·85	4·63	6·65	9·34	10·9	13·9	16·3
45	—	—	—	—	—	2·43	—	—	—	—	—	19·3	—
50	0·80	0·88	0·95	2·01	2·17	3·22	5·50	8·95	13·1	18·9	21·3	26·6	32·1
60	1·33	1·56	1·68	3·65	4·08	—	10·4	17·1	26·7	36·8	40·4	—	60·2
70	2·25	2·75	2·98	6·40	7·26	—	18·5	31·4	49·2	67·2	73·1	—	109·6
80	3·82	4·84	5·26	11·2	—	—	32·3	56·6	—	—	—	—	—
$\Delta_e H$,* (kcal./mole)	(12·8)	(13·1)	(12·9)	(12·8)	(12·8)	—	13·2	13·7	13·9	13·7	13·8	(13·3)	13·5
$\Delta_e S_{298}$ (cal./mole/deg.)	—	—	—	—	—	—	44·4	45·9	46·8	46·0	46·4	44·7	45·4

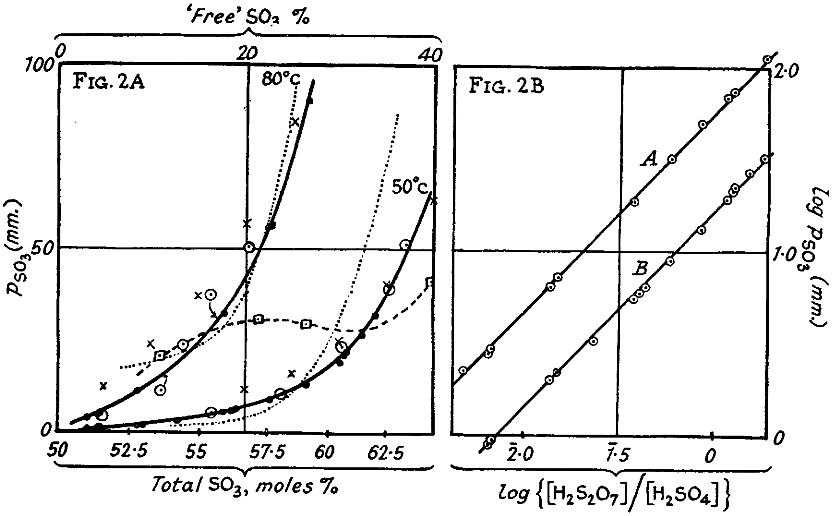
Liquid SO_3, $\Delta_e H = 10·1 - 10·8$ kcal./mole.

* Figures in parentheses relate to a small pressure range and are of lower accuracy.

McDavid's pressure differs from ours, at the same composition, by 20% (Fig. 2A) but at 50°, 60°, and 70° the correspondence is quite close. McDavid's points are scattered on both sides of our isothermals, perhaps owing partly to greater temperature fluctuation (±1°).

Where they overlap, the values of Miles, Niblock, and Wilson are higher than ours, although there is a tendency to converge near the upper limit of the common region of pressure. This is apparent in Fig. 2A, and is discussed further in a later paragraph. At the lowest pressure, Miles's results are slightly erratic (*e.g.*, at 28° the v. p. of 6·9% oleum is recorded as greater than that of 12·7%), and must be a little high on account of the technique adopted with the Bourdon gauge (Table 1) but this effect is insufficient to account for the whole difference. Apparently the optimal range of the apparatus was for pressures of the order of 100 mm., and the temperature variation of pressure, which was evaluated from the higher pressures, agrees substantially with ours.

FIG. 2. *Vapour pressure of oleum as a function of composition.*



○ McDavid.
- - - - - - - I.C.T.
× Miles, Niblock, and Wilson.
--□-- Remy and Meins (40°).
● This paper.

A, slope, 1·07 (temp. 70°).
B, slope, 1·04 (temp. 50°).

The I.C.T. values do not fit in with the other series, both the shape of the isothermals and the temperature variation being different. The data are interpolated at regular intervals of oleum concentration and have almost certainly been smoothed with the assistance of the $\log p - 1/T$ plots. A different situation is presented by the recent results of Remy and Meins, which are very much higher than any other series and are the most difficult of all to understand. The authors state that, with the apparatus at thermal equilibrium, the pressures read with rising temperature were lower than with falling temperature, and that this behaviour was reproduced if the temperature was re-cycled. The question of whether the same limiting pressure was reached when equilibrium was approached from a higher or lower temperature was not discussed by earlier workers, but no differences were observed in our measurements (see Experimental section) and this has also been established for a closely related system, $Cl{\cdot}SO_2{\cdot}OH–SO_3$ (Balson and Adam, *Trans. Faraday Soc.*, 1948, **44**, 412). Another anomalous feature in Remy and Meins's account is that, even at room temperature in the range of composition 20—40%, their acids contained an asbestos-like solid, resembling β-SO_3. The solid phase is normally crystalline and is either H_2SO_4 or $H_2S_2O_7$, depending upon composition (Gable, Betz, and Maron, *J. Amer. Chem. Soc.*, 1950, **72**, 1445). Unless the results are fictitious the most reasonable explanation is that the sulphuric acid and sulphur trioxide had failed to reach equilibrium, as suggested by the authors, but it seems doubtful if it is at all possible to reconcile Remy and Meins's values with the present vapour-pressure measurements.

The Molal Heat of Evaporation of Sulphur Trioxide.—Heats and entropies of evaporation were evaluated by the usual equation,

$$-\boldsymbol{R}\,\mathrm{d}(\ln p)/\mathrm{d}(1/\mathrm{T}) = \Delta_e H = T\Delta_e S \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The $\log p - 1/T$ plot is linear for pressures in excess of about 1 mm. (Fig. 3) and the molal heat of evaporation does not change appreciably with composition (Table 2). Both $\Delta_e H$ and $\Delta_e S$ are high relative to the values for pure sulphur trioxide and this is connected with the formation of disulphuric acid in the solution. With the most dilute oleums the logarithmic lines are curved below 1 mm., but the curvature is anomalous in that it corresponds to an apparent diminution of $\Delta_e H$ as the temperature is lowered and it is not certain that the effect is real. Miles, Niblock, and Wilson (*loc. cit.*) also analysed their results by equation (1), but their values of $\Delta_e H$ (11,300—12,500 cal.) are lower than ours, perhaps because their measurements extended to considerably higher temperatures. Miles and his co-workers found that the logarithmic plots were curved at the lowest pressures, but the onset of curvature was at a much higher pressure (*ca.* 30 mm.) than in our experiments. In general, Miles's logarithmic plot of the measurements with dilute oleum only becomes linear near the upper limit of our pressure range, and this corresponds to the fact that the vapour-pressure measurements themselves are in improved agreement in the same region. It being granted that Miles's results are too high at the lower end of his pressure scale, the results of the two series are much more consistent than appears at first sight.

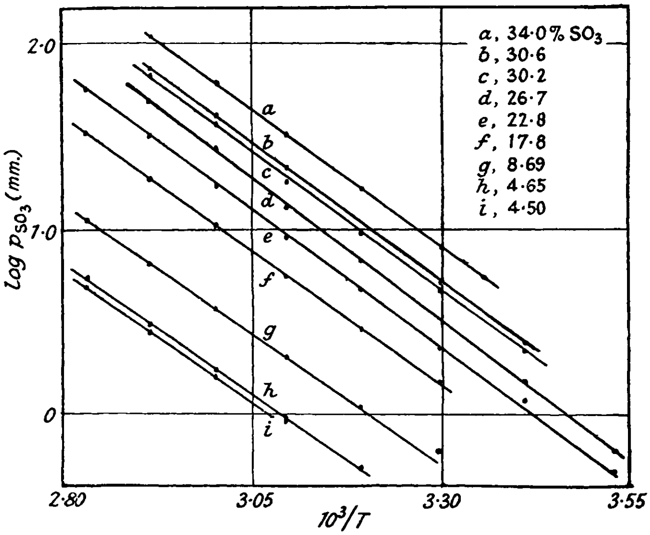


FIG. 3. *Vapour pressure of oleum as a function of temperature.*

The anomalous curvature of the $\log p - 1/T$ plots is probably due to impurities present in the system. In our case about one part per million of sulphur dioxide in the oleum would exert a sufficient pressure to explain the results. Traces of sulphur dioxide were sometimes detected in the oleums but the quantities were too small for analytical estimation. The sulphur dioxide may have distilled with the sulphur trioxide, in spite of precautions, or it may have been produced by decomposition of the sulphur trioxide when the apparatus was sealed-off. A gauge of the self-degassing type may be essential at the lowest pressures.

The I.C.T. measurements give different results. The logarithmic plot is linear for all concentrations of oleum, but the values of $\Delta_e H$ change from 18,000 to 11,000 cal. in the concentration range 9—40%. This is so different from the other evidence that the pressures, particularly with the most dilute media, must be seriously in error. According to Remy and Meins, on the other hand, the logarithmic plot is always curved and $\Delta_e H$ varies from 0 to 8000 cal. Because the heat of evaporation of liquid sulphur trioxide is about 10·5 kcal., this result means that liquid sulphur trioxide should mix *endothermally* with oleum, a conclusion which is contrary to all other evidence (including direct thermal measurements) and seems to be a decisive objection to Remy and Meins's values. It is worth noting that the authors were, apparently, unaware of the I.C.T. data and of the paper by Miles and his co-workers, and that they did not themselves evaluate $\Delta_e H$ from their results.

The heat of evaporation of sulphur trioxide from oleum has been determined by two thermal methods (Miles, Niblock, and Smith, *Trans. Faraday Soc.*, 1944, **40**, 281). A direct measurement was possible with oleums stronger than about 20% by allowing sulphur trioxide to evaporate under reduced pressure, heat being supplied to maintain constant temperature. Weaker oleums were not examined because the vapour pressure was too low and the evaporation very slow. In the range 20—30%, this experiment yielded values about 1000—1500 cal. higher than those in Table 2. The difference may be purely experimental but the thermal method is possibly open to the criticism that the rate of evaporation was small, and the result may therefore lie between the energy of activation for evaporation and the equilibrium value for $\Delta_e H$. In the second method $\Delta_e H$ was evaluated indirectly from the partial molal heat of solution of liquid sulphur trioxide in oleum and the molal heat of evaporation of liquid sulphur trioxide. However, liquid sulphur trioxide does not attain equilibrium if the preparation is intensively dried (and this was the case), and the heat content consequently varies by about 400 cal.; and, in addition, the molal heat of evaporation is uncertain for experimental reasons by the same amount. When this is taken into account, the second measurement gives $\Delta_e H = 14,300 \pm 500$ cal., which is intermediate between the results of the first thermal method and the vapour-pressure values but is in better agreement with the former. Bearing in mind the extent to which the earlier values are conflicting, however, the results in Table 2 seem to be satisfactory in terms of the only thermodynamic test that can be applied to them.

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