456. *The Condensed Phases of Sulphur Trioxide. Part I. Vapour Pressure and Viscosity of the Liquid Phase at Low Temperatures.*

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The vapour pressure and the viscosity of liquid sulphur trioxide have been measured in the range 17—50° C, and results previously reported have been critically reviewed. The following interpolation equations have been derived:

$$\log_{10} p \text{ (mm.)} = 7{\cdot}8663 - 1158{\cdot}9/(t + 188{\cdot}00) \text{ and}$$

$$\log_{10} \eta \text{ (cp.)} = -1{\cdot}3726 - (404{\cdot}82)\, T^{-1} + (2{\cdot}6583)10^5 T^{-2}$$

where t is expressed in °C and T in °K. Calculated values of the molar latent heat of evaporation show a continuous decrease from 10·5 kcal. at 20° to 9·6 kcal. at 50°. The variations of latent heat and of vapour pressure with temperature are discussed for the case of associated liquids, and the behaviour of sulphur trioxide is compared with that of dinitrogen tetroxide and of acetic acid.

INDUSTRIAL demand for liquid sulphur trioxide has focused attention on the complex nature of the condensed phases of this compound, and on the uncertainties about some of the values of its basic physical properties.[1]

There are at least three solid phases: γ-SO_3 consists mainly of cyclic trimer with possibly some monomer present; β-SO_3 consists of polymeric molecules arranged in helical chains of unknown length; and α-SO_3 is a polymer which has defied structure analysis, but in view of its higher melting point, it may have a cross-linked structure.

The liquid phase is an equilibrium mixture of monomer and trimer. Walrafen and Young,[2] from Raman spectra observations, suggest that about 20% exists as trimer at 25°. This, however, should be compared with the claim of Gillespie [3] and his co-workers that liquid sulphur trioxide consists mainly of the trimer at room temperature.

The gas phase is entirely monomeric at high temperatures and normal pressures. At low temperatures, the degree of association in the saturated vapour is relatively slight.

The varying states of molecular aggregation of sulphur trioxide are not unexpected when one considers the isoelectronic analogues, such as the metaphosphate ion, PO_3^-, and the metasilicate ion, SiO_3^{2-}. These also exist as cyclic trimers, *e.g.*, $(Si_3O_9)^{6-}$, as well as in polymeric chains and cross-linked structures. It is noteworthy that there is no evidence for the existence of sulphur trioxide in larger ring structures, such as exist in the 8-membered ring $(P_4O_{12})^{4-}$ or the 12-membered ring $(Si_6O_{18})^{12-}$.

Precise physicochemical measurements on the condensed phases of sulphur trioxide have undoubtedly been hindered by its ready polymerisation at room temperature, a polymerisation which is catalysed by traces of moisture and which may occur to varying and uncertain extent. The inhibition of this polymerisation has recently been reviewed by Bevington and Pegler.[1] The considerable work reported in the patent literature is largely empirical.

The present study was undertaken to investigate the mechanism of polymerisation of liquid sulphur trioxide, but uncertainties were immediately apparent about the physical properties of the liquid state. Preliminary work was therefore carried out on the vapour pressure and viscosity of the liquid.

EXPERIMENTAL

The sulphur trioxide was supplied in 200-g. sealed glass ampoules by the Imperial Smelting Corporation, and had been prepared by a double distillation from oleum to which a little

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[1] Bevington and Pegler, *Chem. Soc. Special Publ.*, 1958, no. 12, 283.

[2] Walrafen and Young, *Trans. Faraday Soc.*, 1960, **56**, 1419.

[3] Gillespie and Oubridge, *Proc. Chem. Soc.*, 1960, 308.

potassium permanganate had been added to remove sulphur dioxide. Chemical analysis of the samples supplied showed less than 0·05% of dioxide, and after distillation *in vacuo* as described below, the content of dioxide was reduced to less than 0·005%. The amount of water present is much more uncertain since the quantitative determination of traces of moisture in sulphur trioxide is very difficult. It is generally accepted that some indication of the dryness of sulphur trioxide is given by its stability towards polymerisation.[1] The procedure described below produced final samples which could be frozen, and remelted at room temperature, two or three times before polymerisation occurred. This is a relatively high stability (in the absence of any added inhibitor) and must imply a correspondingly low moisture content; certainly $<0·1\%$ and possibly $<0·01\%$.

Purification and handling of the sulphur trioxide was carried out in a vacuum system in which the sulphur trioxide was never in contact with any material except glass. The apparatus and the subsequent purification procedure were very similar to those of Smits and Schoenmaker.[4] The apparatus was baked out at 10^{-5} mm., and then the sulphur trioxide was triply distilled *in vacuo*, only the middle fraction of each distillation being collected. The weight of the final purified sample was 10—20 g. (from 200 g.).

Vapour pressures were determined with a glass-spiral Bourdon gauge which was used as a null device and was capable of detecting a pressure difference of 0·1 mm. Viscosity measurements were made with a sealed-capillary tube viscometer, so designed that submerged discharge from the capillary was obtained. Times of flow were reproducible to ±0·1%, and there was no apparent kinetic correction. The viscometer was calibrated with water and the calibration checked against two other liquids. For all measurements, temperature control was achieved with a thermostatic water-bath and the temperature was measured to ±0·02° c.

t	p (mm.)	η (cp.)	L (kcal./mole)
17°	165	2·458	
20	197	2·185	10·47
25	265	1·820	10·31
30	353	1·524	10·16
35	468	1·288	10·01
40	608	1·103	9·86
45	787	0·944	9·71
50	992		9·57

These values of vapour pressure and viscosity are experimental values interpolated without "smoothing" to the exact temperature stated. Experimental measurements were always made within 0·2° of these temperatures.

Vapour Pressure.—Over forty values of the vapour pressure were recorded in the range 17—56° with temperature rising and falling. After allowance for temperature equilibration at any one temperature, there was no change of vapour pressure with time. This confirms the results of previous workers that the equilibrium between monomer and trimer in the liquid is established rapidly. The liquid remained clear and free from polymer throughout the period.

The plot of the two-constant Clausius–Clapeyron equation, $\log p = a - b/T$, showed a negative value of db/dT. The results were therefore fitted to the three-constant Antoine equation, and the constants calculated by the method recommended by Thompson.[5] The vapour pressure at t° c is given by:

$$\log_{10} p\ (\text{mm.}) = 7·8663 - 1158·9/(t + 188·00)$$

The average deviation of the experimental values from this equation is ±0·4%. This deviation is equivalent to errors in the pressure measurement varying from 0·6 mm. at the lower to 5 mm. at the higher pressures, or errors in the temperature measurement of 0·1°.

These errors are somewhat greater than expected, but a check of the above equation by a plot of the deviation curve did not show continuous "drift," or "bowing," or completely random scatter. In fact the deviation curve was of a cyclic form, showing zero deviation at about 20°, 32°, and 50° and maxima of opposite sign at intermediate temperatures.

The normal boiling point interpolated from these vapour-pressure values is 44·45 ± 0·15° c.

Previous measurements of the vapour pressure in this temperature range have been reported

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[4] Smits and Schoenmaker, *J.*, 1924, **125**, 2554.

[5] Thompson, *Chem. Rev.*, 1946, **38**, 1.

by Berthoud,[6] Smits and Schoenmaker,[4] Grau and Roth,[7] and Miles, Niblock, and Wilson.[8] No two sets of results show consistent agreement, differences of 20 mm. at any one temperature being not uncommon. Our values at any given temperature almost always lie between the extremes of values previously reported. All the above workers fitted their results to a two-constant vapour-pressure equation, and in all cases the average deviations from their reported equations are greater than ±1%.

Latent Heat.—Values of the latent heat of evaporation at 5° intervals were calculated by application of the Clapeyron equation and use of the vapour-pressure equation above. Thus,

$$L = \Delta z \boldsymbol{R}T^2 (\mathrm{d}\ln p/\mathrm{d}T) = \Delta z\,(4{\cdot}5757)(1158{\cdot}9)T^2/(t + 188)^2 \text{ cal./mole}$$

where $\Delta z = (pV_g/\boldsymbol{R}T) - (pV_l/\boldsymbol{R}T)$ and V_g and V_l are the molal volumes of saturated vapour and liquid, respectively. V_g was calculated from the Berthelot equation of state by using Berthoud's[6] values of the critical constants, $p_c = 83{\cdot}8$ atm., $T_c = 491°$ K. Values of Δz decreased from 0·992 at 20° to 0·978 at 50°.

The only calorimetric measurement of the latent heat is that of Grau and Roth[7] who reported a value of 10 kcal. at the normal boiling point with the admitted possibility of a large experimental error. Miles, Niblock, and Smith[10] made much more precise calorimetric determinations of the heat of evaporation of sulphur trioxide from high-strength oleums at 30° and found a limiting value of 10·3 kcal./mole at high concentrations of sulphur trioxide.

The temperature coefficient of the latent heat at 25° C being considered, $\mathrm{d}L/\mathrm{d}T \approx C_p$ (gas) − C_p (liquid) = −31 cal. deg.$^{-1}$ mole^{-1}; the value for sulphur trioxide (gas)[9] being taken as C_p = 12 cal. deg.$^{-1}$ mole^{-1} (which assumes no association in the gas phase) it follows that for sulphur trioxide (liquid) at 25°, C_p = 43 cal. deg.$^{-1}$ mole^{-1}.

There is no reported calorimetric measurement of the specific heat of liquid sulphur trioxide, but Miles, Niblock, and Smith[10] measured this quantity for oleums of varying content of trioxide, and extrapolation of their results to 100% sulphur trioxide gives a value of *ca.* 60 cal. deg.$^{-1}$ mole^{-1}. Acceptance of this higher figure would imply that our results underestimate the decrease of latent heat with rise in temperature.

In view of this discrepancy and of the uncertainty in estimation of the volume of the saturated vapour if there is slight association, it is difficult to assess the possible error in our calculated values of latent heat. However, in the absence of precise calorimetric measurements, we feel that our values are more reliable than any previously reported.

Viscosity.—Values of the absolute viscosity were determined at 5° intervals in the range 17—50° C. There was no indication of change of viscosity with time at any temperature, nor was there any trace of polymer at any time during the measurements. The density values used to calculate the absolute viscosities were the mean of those of Berthoud[6] and of Lichty.[11]

The following equation expressed the viscosity at T °K:

$$\log_{10}\eta\ (\text{cp.}) = -1{\cdot}3726 - (404{\cdot}82)T^{-1} + (2{\cdot}6583)10^5T^{-2}$$

The average deviation of experimental values from this equation is ±0·15%, which is within the estimated experimental error.

Previous measurements of the viscosity of liquid sulphur trioxide have been reported by Luchinskii,[12] and by Amelin, Illarionov, and Borodastova.[13] The results of the former are far too high because of inadequate purification of the sample. The agreement between our results and those of Amelin *et al.*, who used a vacuum-distillation technique, is within 0·5% at the lower temperatures and within 2% at 50°, our figures being generally higher, though the results of the Russian workers show more "scatter."

Amelin *et al.*[13] commented on the fact that a plot of log η against $1/T$ was not linear, and our findings confirm this. On the basis of the simple equation, $\eta = A \exp(E/\boldsymbol{R}T)$, this can be interpreted in terms of a variation of E with temperature. At the normal boiling point, it

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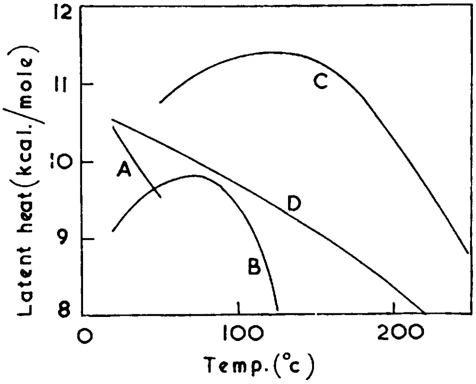
[6] Berthoud, *Helv. Chim. Acta*, 1922, **5**, 513.
[7] Grau and Roth, *Z. anorg. Chem.*, 1930, **188**, 173.
[8] Miles, Niblock, and Wilson, *Trans. Faraday Soc.*, 1940, **36**, 345.
[9] Stockmayer, Kavanagh, and Mickley, *J. Chem. Phys.*, 1944, **12**, 408.
[10] Miles, Niblock, and Smith, *Trans. Faraday Soc.*, 1944, **40**, 281.
[11] Lichty, *J. Amer. Chem. Soc.*, 1912, **34**, 1440.
[12] Luckinskii, *Zhur. fiz. Khim.*, 1938, **12**, 280.
[13] Amelin, Illarionov, and Borodastova, *Zhur. fiz. Khim.*, 1951, **25**, 542.

can be calculated that $E = 5{\cdot}79$ kcal./mole and the ratio $L/E = 1{\cdot}68$. The low value of this ratio is consistent with the view that sulphur trioxide is an associated liquid.

DISCUSSION

Latent Heat of Evaporation of an Associated Liquid.—The latent heat of evaporation of sulphur trioxide shows a marked decrease with rise in temperature and is certainly not constant as was suggested by Smits and Schoenmaker. With a normal liquid the latent heat decreases continuously with rise in temperature, becoming zero at the critical point. A substance which is associated in the liquid and the vapour phase will not necessarily exhibit this continuous decrease and the latent heat may pass through a maximum. Dinitrogen tetroxide and acetic acid both provide examples of maxima in the latent heats of evaporation, as shown in the Figure. These curves have been calculated by application of the Clapeyron equation to the recorded vapour-pressure and specific-volume data.[14] The curve for water is shown for comparison.



Variation of latent heat of evaporation with temperature.

A, *Sulphur trioxide.*
B, *Dinitrogen tetroxide.*
C, *Acetic acid dimer.*
D, *Water.*

The form of these curves is readily explicable in terms of the changing degrees of molecular association in the two phases. Consideration of an isothermal cycle involving the associated and dissociated species in both phases, as described by Gray and Rathbone [15] for dinitrogen tetroxide, gives for the latent heat of evaporation per formula weight of associated species:

$$L = L_n + \alpha\Delta H_g - \beta\Delta H_l$$

L_n is the hypothetical latent heat of evaporation of the fully associated liquid to give a fully associated vapour, ΔH_g and ΔH_l are the enthalpies of dissociation and α and β the degrees of dissociation in the vapour and the liquid phase, respectively.

Therefore at temperatures where the liquid is largely associated but the vapour is becoming increasingly dissociated a positive temperature coefficient of the latent heat may be observed, as shown by dinitrogen tetroxide and acetic acid in the lower temperature region; whereas in the case of a largely-dissociated vapour in equilibrium with an increasingly dissociated liquid, a large negative temperature coefficient will result, as in the case with sulphur trioxide at 25° and with the above two liquids at higher temperatures.

Vapour Pressure of an Associated Liquid.—Deviations from the two-constant vapour-pressure equation, $\ln = a - b/T$, can be discussed in terms of db/dT where $b = L/\Delta z$ the symbols having the same significance as before. For normal liquids at low vapour

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[14] Reamer and Sage, *Ind. Eng. Chem.*, 1952, **44**, 185 (for dinitrogen tetroxide); Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier, London, 1950 (for acetic acid).

[15] Gray and Rathbone, *J.*, 1958, 3550.

pressures, db/dT must always be negative, but at high pressures when both gas non-ideality and the volume of the liquid phase become increasingly significant, experiments show that for some liquids db/dT becomes positive. This effect is indicated by a point of inflection in a plot of the two-constant equation as the critical point is approached.[16] Most empirical vapour-pressure equations (including the Antoine equation) cannot represent such behaviour, and caution is always necessary in the " smoothing " of experimental measurements of high vapour pressures.

Superficial consideration of the vapour pressure of a substance which is associated in the vapour phase might lead to the expectation of even larger deviations from the two-constant equation. Application of the ideal gas equation to the saturated vapour would be manifestly incorrect if the degree of dissociation is changing with temperature. However, such an effect would also be reflected in the increase of latent heat with temperature so that db/dT would not be abnormally large, and experiment confirms that the two-constant equation is still a reasonable approximation in these cases.

These considerations are relevant to any assessment of the reliability of literature values of the vapour pressure of sulphur trioxide at higher temperatures. Above 60° the only recorded measurements are those of Smits and Schoenmaker [17] up to 90°, and of Berthoud [6] from 98° to the critical temperature, 218°. There are marked discrepancies between the two sets even though no overlapping occurs. For example, extrapolation of Smits and Schoenmaker's results gives a vapour pressure of 10·5 atm. at 98·2° compared with Berthoud's observed value of 9·2 atm. In addition, Smits and Schoenmaker's results apparently fit the two-constant vapour-pressure equation with only random scatter in the range 17—90°, whereas Berthoud's values in the range 98—218° give a definite positive value of db/dT, an effect which would necessitate a marked point of inflection in a plot of the two-constant equation.

The only recorded values for the critical pressure and critical volume are those of Berthoud.[6] Schenk [18] however measured the critical temperature and his value agrees with that of Berthoud to within 2°. It is obvious that confirmatory values are required for the vapour pressure of sulphur trioxide at high temperatures and for the critical constants, and an apparatus for that purpose is now under construction.

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[16] Reid and Sherwood, " The Properties of Gases and Liquids," McGraw-Hill, New York, 1958, p. 72.

[17] Smits and Schoenmaker, *J.*, 1926, 1108.

[18] Schenk, *Annalen*, 1901, **316**, 1.