937. *The Condensed Phases of Sulphur Trioxide. Part II.*[1] *Vapour Pressure of the Liquid at Temperatures up to the Critical Point.*

By D. C. ABERCROMBY and P. F. TILEY.

An apparatus is described which is suitable for the study of corrosive liquids in the range 50—250°c and 2—100 atm. pressure. The apparatus embodies a glass helical gauge mounted in a small autoclave fitted with observation windows. Vapour pressures in the range 60—210°c are reported for liquid sulphur trioxide, and an interpolation equation for 80—200°c is: $\log_{10} p(\text{atm.}) = 4\cdot2719 - 945\cdot78/(t°c + 180)$. The critical temperature and pressure are reported as 217·7°c and 80·8 atm. which are not seriously divergent from accepted values, but the vapour pressures recorded in the region of 100°c are more than 10% lower than currently accepted figures.

THE recorded values of vapour pressure for liquid sulphur trioxide above 2 atm. display considerable anomalies,[1,2] and a published vapour pressure–temperature graph[3] shows a marked discontinuity in the curve. Therefore a new series of measurements have been made with an apparatus designed for studying the behaviour, at temperatures and pressures up to 250°c and 100 atm., of liquids which attack metals but are inert to glass.

EXPERIMENTAL

Apparatus.—The apparatus comprised four separate units: a glass helical gauge; a small autoclave with observation windows; a pressure manifold; and an air thermostat, the first two units are shown in the Figure. The glass gauge (1½ in. diam. by 6 in.) was sufficiently
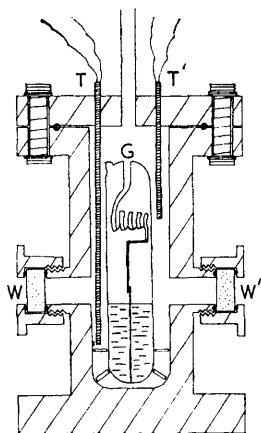
Apparatus for the measurement of vapour pressure. G, glass gauge; W,W', quartz windows; T,T', thermo-junctions.

robust to withstand a pressure difference of 1½ atm., and was sensitive to 0·01 atm. The zero-point of the gauge was insensitive to change of temperature in the range studied. The autoclave was constructed of ½ in. mild steel and contained two circular fused-quartz observation windows (½ in. aperture and ½ in. thick) which were mounted with silicone rubber O-ring seals. The temperature in the autoclave was indicated by two sheathed copper–constantan thermo-junctions connected by continuous wires to two similar junctions at 0°c; the series assembly of two thermocouples was calibrated *in situ*, the e.m.f. being measured to ±1 μv. The precision of the temperature measurement was ±0·02°c and the accuracy of the calibration was ±0·1°c.

The balancing pressure on the outside of the gauge was supplied from a nitrogen cylinder, and was controlled by needle valves; it was measured by high-precision Bourdon gauges which were calibrated against a dead-weight pressure balance for both increasing and decreasing

[1] Part I, Hyne and Tiley, *J.*, 1961, 2348.
[2] Bevington and Pegler, *Chem. Soc. Special Publ.* No. 12, 1958, 283.
[3] Duecker and West, " Manufacture of Sulphuric Acid," Reinhold, New York, 1959, p. 451.

pressures. The precision and accuracy of the readings were ± 0.02 atm. below, and ± 0.1 atm. above, 12 atm. The air thermostat was a thermostatically controlled oven with a circulating fan; random fluctuations of the air temperature in the oven were about $2°c$ but these were attenuated within the autoclave (mass 50 kg.) to less than $0.1°c$.

Procedure.—Purified sulphur trioxide was distilled *in vacuo* as previously described,[1] the final fraction (80 g. from 200 g.) being collected in the glass gauge to give approximately a critical filling. The gauge was sealed, removed from the vacuum train, and subsequently mounted in the pressure vessel, which was then assembled in the oven and connected to the manifold. The whole apparatus was kept behind a safety wall, the gauge pointer being observed through a telescope and mirror assembly. Continual adjustment of the balancing pressure as the temperature increased maintained a null reading of the glass gauge; this procedure ensured that no part of the glass suffered any undue pressure difference. Readings were taken at $5°c$ intervals, after having allowed adequate time for temperature equilibration. One obvious disadvantage of the technique was the need for continuous close attention by the operator, a disadvantage which could be overcome by embodying automatic control valves such as those used by Nordwall and Jones [4] in a related, but much more complex, apparatus.

The glass gauge itself was too large to allow an accurate measurement of the critical temperature, although a striking example of critical opalescence was observed on cooling from $220°$ to $213°c$. The critical temperature was measured by the " disappearing meniscus " technique, with liquid samples (purified as before) in 3—5 cm. lengths of 2 mm.-bore glass tube. Separate experiments were performed with the tubes mounted in a solid aluminium block inside the autoclave, in order to eliminate any temperature gradients which might occur under non-equilibrium conditions. The rate of change of temperature through the critical point was about $0.2°c/hr.$, and the meniscus disappeared and re-appeared within a recorded range of $0.10°c$

RESULTS AND DISCUSSION

Forty-eight pressure readings were recorded in the range 59—224°c; the Table shows values interpolated at $10°$ intervals without " smoothing," readings having been taken within $2°$ of all the temperatures quoted.

t (°c)	60	70	80	90	100	110	120	130
p (atm.)	2·01	2·98	4·26	5·91	7·90	10·27	13·20	16·61
t (°c)	140	150	160	170	180	190	200	210
p (atm.)	20·57	25·30	30·67	36·88	44·12	52·19	61·42	71·80

Critical temperature $217.7 \pm 0.2°c$. Critical pressure 80.8 ± 0.3 atm.

Three different samples were used for the vapour-pressure measurements with a reproducibility of $\pm 0.4\%$ over the whole range. The normal boiling point of the final sample was determined by mounting the gauge in a water thermostat, and was recorded as $44.6° \pm 0.1°c$. In the region of overlapping readings (50—65°c), the results agree, within experimental error, with those of Hyne and Tiley [1] who reported the boiling point as $44.45° \pm 0.15°c$.

An Antoine equation, $\log_{10} p(\text{atm.}) = 4.2719 - 945.78/(t°c + 180)$, fits the results in the range 80—200°c with an average deviation of $\pm 0.5\%$ of p, the deviations lying on a smooth cyclic curve with values of -0.9% at 80°c, $+0.8\%$ at 100°c, -0.9% at 150°c, and $+1.2\%$ at 200°c. Use of the above equation may be extended down to 60°c by subtraction of a term, $10^{-4}(80 - t)^2$. An Antoine equation can be fitted over the range 30—218°c but the maximum deviation increases to 2·5—3% and the deviation curve is still of a cyclic form. The cyclic nature of the deviation curve, and the fact that the deviations are greater than the experimental error, show that incautious use of an Antoine equation may do injustice to the precision of experimental results.

If these results are plotted on log p against $1/T$ (T in °K) co-ordinates, a continuous curve is obtained which is concave to the $1/T$ axis over most of the temperature range, with a tendency to inflexion near the critical point. This kind of deviation from the linearity predicted by the Clapeyron–Clausius equation is characteristic of nearly all

[4] Nordwall and Jones, Report (unclassified) R. 3565, U.K.A.E.R.E., Harwell, 1961.

liquids,[1] although in the case of sulphur trioxide the deviation is greater than normally observed. This is evident from the fitting of the results to an Antoine equation, which in this case requires a constant of 180°c compared with a normal value for most liquids of about 230°c; a linear Clapeyron–Clausius plot would be obtained if the constant were 273·16°c.

Gray and his co-workers [5] have analysed theoretically the vapour pressure curves of associated liquids such as dinitrogen tetroxide, acetic acid, and hydrogen fluoride, and concluded that the deviations from an equation of Clapeyron–Clausius form are lower for these liquids than for normal ones, and may even be in the opposite sense, *i.e.*, the Antoine constants are greater than 230°c, and may be greater than 273°c. However, although sulphur trioxide is partially associated as trimeric molecules in the liquid state, the vapour is almost completely dissociated, and the cases discussed by Gray are all those of partially dissociated vapours in equilibrium with largely associated liquids. This difference between sulphur trioxide and the other compounds mentioned has already been demonstrated in the behaviour of the latent heats of evaporation.[1]

These results for the vapour pressure of sulphur trioxide throw doubt on some previously reported data, *e.g.*, Berthoud's [6] values in the range 98—218°c, which cannot be combined with the low-temperature values in a continuous curve when plotted on log p, $1/T$ co-ordinates. Our vapour-pressure values indicate that Berthoud's results in the region of 100°c are 10—15% high, but this discrepancy decreases to less than 2% above 150°c. It seems likely that the particular technique of pressure measurement (that of Pellaton [7]) used by Berthoud was, in this case, susceptible to large errors at the bottom of the range. The results of Smits and Schoenmaker,[8] which give an exactly linear log p vs. $1/T$ (°K) relationship from 20° to 90°c, are 15—25% higher than our figures at 70—90°c, but as no details of experimental technique are reported for measurements above 2 atm. this large divergence remains inexplicable. It is noteworthy that our vapour-pressure results confirm (generally within 1%) the values quoted in the International Critical Tables.[9] These values could only have been obtained by a very drastic " smoothing " of the experimental results known at that time; a more modern compilation [10] of vapour-pressure data is less in accordance with our results in the range 80—120°c.

BRISTOL COLLEGE OF SCIENCE AND TECHNOLOGY,
            ASHLEY DOWN, BRISTOL 7.   *[Received, February 26th, 1963.]*

[5] Armitage and Gray, *Trans. Faraday Soc.*, 1962, **58**, 1746; Armitage, Gray, and Wright, *J.*, 1963, 1796.
[6] Berthoud, *Helv. Chim. Acta*, 1922, **5**, 513.
[7] Pellaton, *J. Chim. phys.*, 1915, **13**, 426.
[8] Smits and Schoenmaker, *J.*, 1926, 1108.
[9] Cragoe, " International Critical Tables," McGraw-Hill, New York, 1928, Vol. III, p. 228.
[10] " Handbook of Chemistry and Physics," ed. Hodgman, Chemical Rubber Publ. Co., Cleveland, 1961, p. 2390.