

153. *The Determination of the Surface Tension and Viscosity of Liquid Chlorine Trifluoride.*

By A. A. BANKS, A. DAVIES, and A. J. RUDGE.

The surface tension of liquid chlorine trifluoride has been determined by the method of capillary rise over the temperature range 0—50°. The results are expressed by the equation $\gamma_t = 26.7 - 0.16t \pm 0.2$ dyne/cm. The parachor for chlorine trifluoride is 111.5. The viscosity of chlorine trifluoride has been measured over the temperature range 18—50°, the value at 20° being 4.35 mP.

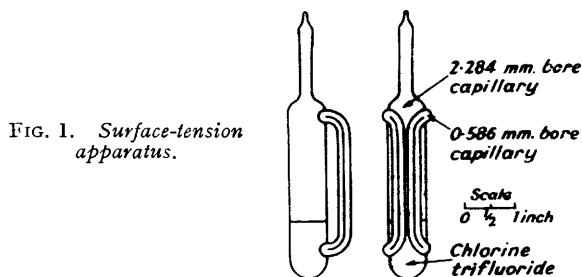
INFORMATION on the physical properties of chlorine trifluoride is incomplete. In particular, there are no data on the surface tension or the viscosity. We have measured these two properties for the compound prepared and purified as described by Banks and Rudge (*J.*, 1950, 191). Work in this laboratory has shown conclusively that, contrary to Ruff and Krug's statements (*Z. anorg. Chem.*, 1930, **190**, 270), neither liquid nor gaseous chlorine trifluoride reacts with dry glass when free from traces of hydrogen fluoride, Pyrex glass

showed no signs of etching after 10 hours' contact with liquid chlorine trifluoride or with its vapour at 50°.

The surface tension has been calculated from measurements of the difference in rise of the liquid in glass capillaries which, to minimise errors arising from optical distortion, were sealed externally to the reservoir (Fig. 1). The results obtained are given in the following table, the calculated values being obtained from the equation $\gamma_t = 26.7 - 0.16t \pm 0.2$

γ , dyne/cm. :				γ , dyne/cm. :					
	Obs.	Calc.	$\Delta\gamma$	$100(\Delta\gamma)^2$	t	Obs.	Calc.	$\Delta\gamma$	$100(\Delta\gamma)^2$
0.0°	26.6	26.7	-0.1	1.0	25.5°	22.7	22.6	0.1	1.0
2.5	26.3	26.3	0	0	25.6	22.8	22.6	0.2	4.0
4.0	26.0	26.1	-0.1	1.0	31.0	22.2	21.7	0.5	25.0
8.9	25.35	25.3	0.05	0.2	37.6	20.4	20.7	-0.3	9.0
9.0	25.15	25.3	-0.15	2.2	38.0	20.3	20.6	-0.3	9.0
14.6	24.3	24.4	-0.1	1.0	40.4	20.5	20.2	0.3	9.0
18.4	24.05	23.8	0.25	6.2	42.0	20.0	20.0	0	0
20.6	23.1	23.4	-0.3	9.0	47.0	19.1	19.2	-0.1	1.0
21.2	23.3	23.3	0	0.0	49.9	18.7	18.7	0	0
25.1	22.8	22.7	0.1	1.0					

dyne/cm., where γ_t is the surface tension between chlorine trifluoride and its vapour at t° . The R.M.S. deviation of the calculated from the observed values is ± 0.2 dyne/cm.



From Banks and Rudge's values (*loc. cit.*) for the density of liquid chlorine trifluoride and values of the surface tension calculated from the above equation, the parachor for chlorine trifluoride has been calculated to be 111.5, as indicated below, M being 92.5.

t	0°	12°	40°
Surface tension (γ), dyne/cm.	26.7	24.8	20.3
γ^2	2.27	2.23	2.12
Density (ρ_l) of liquid ClF ₃ , g./ml.	1.8853	1.8500	1.7616
Density (ρ_v) of ClF ₃ vapour, g./ml.	0.0027	0.0040	0.0105
$\rho_l - \rho_v$	1.8826	1.8460	1.7511
Parachor, $M\gamma^2/(\rho_l - \rho_v)$	111.6	111.7	111.3

From this value, the parachor equivalent of tervalent chlorine can be calculated. Samuel (*J. Chem. Phys.*, 1944, 12, 167) gives the parachor equivalent of fluorine as 25, and hence that of tervalent chlorine is $111.5 - 3 \times 25 = 36.5$. The parachor equivalents given by Samuel for ter- and quinque-valent phosphorus, bi- and quadri-valent sulphur, and univalent chlorine are listed below together with the present value for tervalent

P ³	37.1	S ²	49.8	Cl ¹	54.3
P ⁵	18.3	S ⁴	29.5	Cl ³	36.5
Difference	18.8		20.3		17.8

chlorine, which is seen to fit reasonably well into the series. (The superscripts denote the valency state in covalent linkage.) This value is uncertain by an amount equal to three times the uncertainty in the value used for fluorine. Desreux (*Bull. Soc. chim. Belg.*, 1935, 44, 249) gives a value of 26.1 for the latter, and this would give a value of 33.2 for the parachor equivalent of tervalent chlorine.

A modified form (Fig. 3) of the closed viscometer described by Plank and Hunt (*J.*

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Amer. Chem. Soc., 1939, **61**, 3590) was calibrated with distilled water and used to determine the viscosity of chlorine trifluoride. The values found are given below, followed by those at the b. p. and at regular intervals of temperature, taken from the graphed results.

t	17.3°	17.7°	19.4°	26.0°	32.65°	36.3°	39.8°	48.0°	
η , mP	4.48	4.47	4.38	4.07	3.80	3.65	3.52	3.23	
t	11.75°	15.0°	20.0°	25.0°	30.0°	35.0°	40.0°	45.0°	50.0°
η , mP	4.78	4.60	4.35	4.12	3.90	3.70	3.51	3.33	3.16

EXPERIMENTAL

The method of mounting the capillaries for the surface-tension measurements is shown in Fig. 1, and the surface-tension apparatus is shown attached to the micrometer and knife edge assembly in Fig. 2. The capillaries were selected from a large stock of tubing after measurement of their internal diameters in two directions at right angles. Those sections of tubing which showed 2% or more ellipticity were rejected. The selected capillaries were tested for uniformity of bore by measurement of the length of a thread of mercury in different parts of the tube. After being fused to the reservoir the capillaries were again checked for uniformity of bore

FIG. 2. Surface-tension apparatus and micrometer assembly.

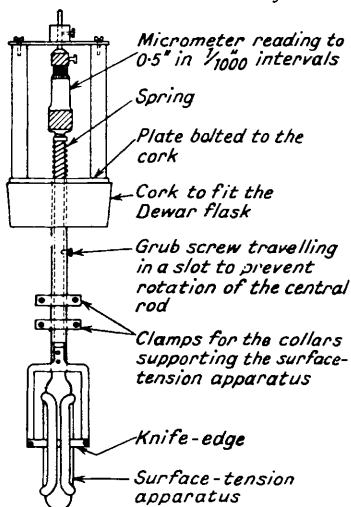
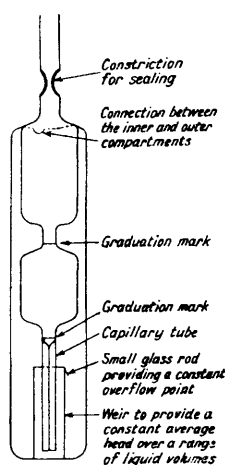


FIG. 3. Sealed viscometer. ($\frac{1}{2}$ scale.)



and their diameters (2.284 and 0.586 mm.) were calculated from the length and weight of the mercury thread.

Before use, the apparatus was cleaned with chromic-sulphuric acid and then steamed for 2 hours. It was dried by heating it *in vacuo*. The surface-tension apparatus was attached to the micrometer assembly by means of two collars as shown in Fig. 2. The assembly fitted into the top of a Dewar flask having a clear strip for observation. A hand-operated stirrer, a mercury-in-glass thermometer (calibrated against an N.P.L. standard) and a small, low-voltage electric heater element were also inserted (not shown in Fig. 2). As a safety measure, carbon tetrachloride was used as the bath liquid. After the whole apparatus had been tilted gently to cause the liquid in the capillaries to wet the walls above the normal level of the meniscus, each meniscus in turn was sighted through a telescope and the knife edge was adjusted by the micrometer screw to the level of the lowest point of the meniscus. The two micrometer readings were recorded and used to calculate the difference in level of the two menisci. This method of measuring the difference in levels was used essentially to minimise any errors caused by optical distortion in the walls of the flask, although the presence of the knife edge also resulted in the image of the meniscus in the telescope being more clearly defined.

As a check on the apparatus and technique, the surface tensions of water and benzene were measured before measurements were carried out on chlorine trifluoride. The water was distilled from alkaline permanganate and from sulphuric acid before being distilled into the apparatus. The benzene was twice recrystallised and dried over sodium. Five determinations were carried out in each case and all the results were within 2% of the accepted values.

The apparatus and method used to fill chlorine trifluoride into the surface-tension apparatus were essentially those used in filling the dilatometers for the density determinations (Fig. 1, Banks and Rudge, *loc. cit.*). The surface-tension apparatus was baked out *in vacuo* before use, and after being filled was sealed off *in vacuo*. Surface tension values were calculated by use of the method and correction tables given by Sugden (*J.*, 1921, 119, 1483).

The viscometer used is shown in Fig. 3 and varies only in details of construction from that described by Plank and Hunt (*loc. cit.*). It was cleaned with chromic-sulphuric acid and was washed with distilled water before being calibrated with distilled water. From the equation $\eta = p\pi r^4 t / 8vl - v\rho / 8\pi l$, where p = mean hydrostatic pressure, r = radius of the capillary, t = time in seconds, v = volume of liquid flowing, l = length of capillary, ρ = density of liquid, and η = viscosity, the equation $at^2 - b = t\eta/\rho$, where a and b are constants of the viscometer, can be derived; t was measured at three different temperatures for water and from two of the values obtained the constants a and b were calculated. The calculations were checked by using these constants to calculate the viscosity of water from the third value of t .

The viscometer was filled with chlorine trifluoride by the method used in filling the surface-tension apparatus. For safety, these measurements were carried out in an aluminium-block thermostat, in the cavity of which the viscometer was a sliding fit. The viscometer was supported at both ends on steel wool and was held in place by an aluminium plug screwed into the open end of the cavity. Two holes drilled through the block, and corresponding holes through the fire brick supporting the heater elements and through the casing of the thermostat, enabled the two etched graduation marks on the viscometer to be observed. The thermostat was mounted on trunnions so that it could be inverted to fill the upper reservoir of the viscometer with chlorine trifluoride. Temperatures were measured with a mercury-in-glass thermometer (calibrated against an N.P.L. standard) fitted into a pocket in the aluminium block. It was realised that the attainment of temperature equilibrium between the block and the liquid in the viscometer would be slow, and an estimate of the time required was made before carrying out the measurements on chlorine trifluoride. 50 Ml. of water were placed in a boiling-tube of similar dimensions to the viscometer and the tube was sealed with a rubber bung carrying a thermometer which dipped into the water. This tube was placed in the cold thermostat which was then switched on set for a temperature of 50°. It was found that at least 3 hours were required before the temperature of the water was within 0.1° of that of the block. During the measurements on chlorine trifluoride the viscometer was kept in the thermostat at the required temperature for 4 hours before readings were taken. A series of readings were taken at each temperature, and the absence of a drift in the observed flow times was an indication that temperature equilibrium had been attained.