43. *The Determination of the Liquid Density of Chlorine Trifluoride.*

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The liquid density of chlorine trifluoride under its own vapour pressure has been determined over the range −5° to +46° in sealed Pyrex glass dilatometers. Contrary to a previous report, pure chlorine trifluoride was found to have no detectable action on dry Pyrex glass. The results are expressed in the equation $d_4^t = 1{\cdot}8853 - 2{\cdot}942 \times 10^{-3}t - 3{\cdot}79 \times 10^{-6}t^2$.

The preparation of chlorine trifluoride was first described by Ruff and Krug (*Z. anorg. Chem.*, 1930, **190**, 270), since when only nine communications (Schmitz and Schumacher, *Z. Naturforsch.*, 1947, **2a**, 362, 363; Domange and Neudorffer, *Compt. rend.*, 1948, **226**, 920; Schäfer and Wicke, *Z. Elektrochem.*, 1948, **52**, 205; Booth and Pinkston, *Chem. Reviews*, 1947, **41**, 421; B.I.O.S. Final Report No. 1595; C.I.O.S. Report No. XXII-17) dealing with this compound have appeared in the literature. Ruff and Krug determined some of the physical properties of chlorine trifluoride, but neither they nor any of the later workers have reported a value for the liquid density.

The present determinations were carried out on chlorine trifluoride which was prepared by direct combination of the elements at 280° and purified by passing the vapour over sodium fluoride pellets to remove hydrogen fluoride and then by distillation *in vacuo* to remove more volatile impurities such as chlorine and chlorine monofluoride. In the absence of a precise method of determining fluorine, chemical estimation of the purity of the chlorine trifluoride used was not undertaken.

The dilatometers were calibrated with distilled water after the measurements on chlorine trifluoride had been made; visual examination of the glass at this stage revealed no etching. In calculating the results, all weighings were reduced to vacuum, and the weight of chlorine trifluoride present as vapour was calculated by the equation

$$\log p = 7{\cdot}42 - 1{\cdot}292 \times 10^3/T$$

given by Ruff and Krug (*loc. cit.*). The density values obtained were fitted to a curve of the type $d = a + bt + ct^2$ by the method of least squares, giving the equation

$$d_4^t = 1{\cdot}8853 - 2{\cdot}942 \times 10^{-3}t - 3{\cdot}79 \times 10^{-6}t^2$$

The experimental results, together with the values calculated from the above equation, are shown in Table I. Table II gives the calculated value of the density of liquid chlorine trifluoride at regular intervals of temperature and at the boiling point. A direct determination of the boiling point has given a value of 12·0° ± 0·1° at 760 mm. of mercury pressure, which is 0·7° higher than that calculated by Ruff and Krug from their vapour-pressure measurements. The determination was carried out in a Pyrex glass apparatus in which pure chlorine trifluoride was refluxed and the condensate allowed to impinge on a thermocouple calibrated against an N.P.L. standard thermometer.

The standard deviation of the calculated values in Table I from the observed values is ±0·0003 g./ml.

Table I.

t.	d (obs.), g./ml.	d (calc.), g./ml.	d (obs.) − d (calc.), 10^{-4}.	$(\Delta d)^2$, 10^{-8}.
−4·07°	1·8970	1·8972	−2	4
1·70	1·8806	1·8803	3	9
9·64	1·8566	1·8566	0	0
12·68	1·8476	1·8474	2	4
20·92	1·8218	1·8221	−3	9
26·90	1·8031	1·8034	−3	9
26·92	1·8036	1·8033	3	9
38·71	1·7654	1·7657	−3	9
38·77	1·7661	1·7655	6	36
45·63	1·7431	1·7431	0	0
				Σ = 89

Table II.

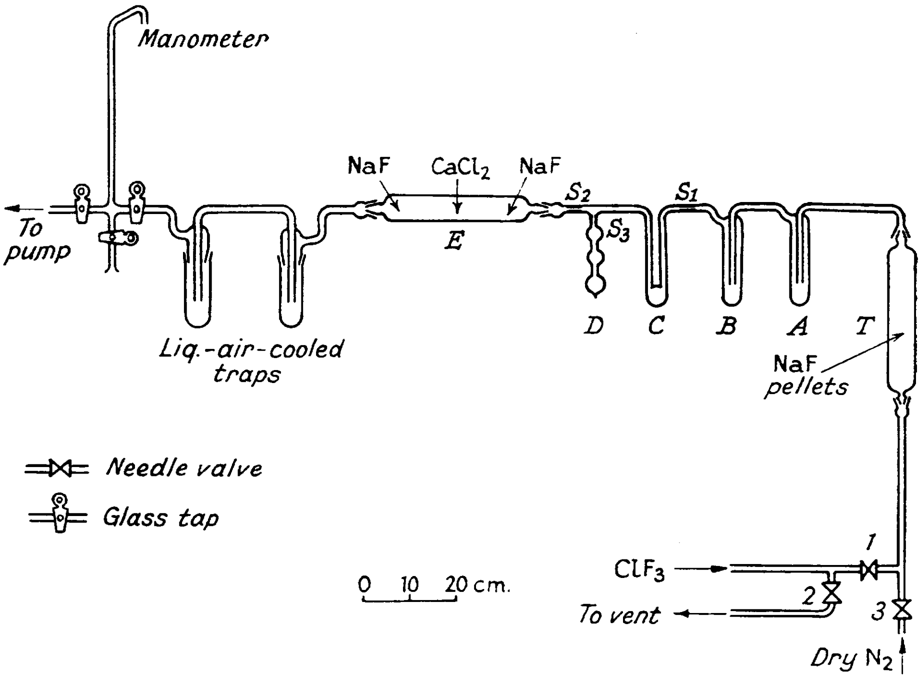
t	0°	10°	12°	15°	20°	25°	30°	35°	40°	45°	50°	60°
d (calc.)	1·8853	1·8555	1·8500	1·8403	1·8249	1·8094	1·7936	1·7777	1·7616	1·7452	1·7287	1·6951

Experimental.

The apparatus used is shown diagramatically in Fig. 1. Except for the three valves (1, 2, and 3), it was constructed entirely of Pyrex glass, the cone joints being sealed with a chloro-fluoro-hydrocarbon wax which had been shown to be inert to chlorine trifluoride vapour at normal temperatures. The valves were Negretti and Zambra needle valves which had been carefully degreased, the gland packings being replaced with asbestos string soaked in a chlorine-trifluoride-resistant chloro-fluoro-hydrocarbon oil. These valves were connected with their seatings towards the apparatus which could therefore be evacuated with the valves closed, without the need for ensuring that the glands were vacuum-tight.

The apparatus was rigorously cleaned and dried before assembly, and all the glassware was baked out *in vacuo* for an hour before use to ensure the complete absence of moisture. Chlorine trifluoride vapour, from a steel cylinder containing the liquid under pressure, was admitted through valve 1, and was diluted with approx. half its volume of dry nitrogen admitted through valve 3. The gas mixture was passed through the hydrogen fluoride absorption tube *T* packed with sodium fluoride pellets, and the chlorine trifluoride was condensed in trap *B* cooled in a solid carbon dioxide–trichloroethylene bath. Trap *A* served to collect any sodium fluoride dust blown from the pellets. When sufficient chlorine trifluoride had been collected in *B*, valves 1 and 3 were closed and the whole apparatus was evacuated. The low-temperature bath was transferred from *B* to *C*, and the chlorine trifluoride was distilled into *C*. During this distillation, any chlorine or chlorine monofluoride, together with a little chlorine trifluoride passed to the calcium chloride tube *E* which served to destroy the fluorides, and chlorine was collected in the traps cooled in liquid air. The trap *C* and dilatometer *D* were sealed off *in vacuo* as a unit at the constrictions S_1 and S_2.

FIG. 1.



The liquid chlorine trifluoride was allowed to warm to room temperature and, by tilting, sufficient chlorine trifluoride was poured into the dilatometer (shown in detail in Fig. 2*A*) to fill it to the required level at the temperature at which measurement was to be made. The dilatometer and trap were then simultaneously cooled in solid carbon dioxide, and the dilatometer was isolated by sealing off at S_3. During cooling of the dilatometer with the trap attached, chlorine trifluoride tended to distil from the dilatometer back to the trap because of the faster cooling of the trap with its smaller volume of liquid. To overcome this, the type of dilatometer shown in Fig. 2*B*, which permits sufficiently accurate adjustment of the quantity of chlorine trifluoride to be made at −78°, was used in the later determinations. By extrapolation of the density results already obtained, the two bulbs were made of such volumes that when the lower bulb was filled with chlorine trifluoride at −78°, the amount of chlorine trifluoride present was sufficient to fill both bulbs at the temperature at which it was intended to carry out the determination.

The thermostat used consisted of a Dewar flask with clear observation strips, filled with dry carbon tetrachloride. This liquid was used in preference to water as a safety precaution, as it had been shown to be stable to chlorine trifluoride up to at least 80°. Temperature control above room temperature was obtained by manual operation of a variable-voltage power pack supplying current at 0—15 volts to a small heating coil immersed in the carbon tetrachloride which was rapidly stirred. A maximum of 3 watts power input was required to maintain the highest temperature used. For temperatures below room temperature, cooling was effected and maintained by the addition of small pieces of solid carbon dioxide. The temperature was measured with a Beckmann thermometer calibrated against a set of N.P.L. standard thermometers. The dilatometer was supported in the thermostat by means of a rigid wire cradle in such a position that the cathetometer measurements were made through a section of the unsilvered strip previously shown to have the minimum optical distortion. The dilatometer was maintained for ½ hour at the temperature (±0·01°) required to bring the chlorine trifluoride meniscus to the centre of one of the lengths of uniform-bore capillary tubing. The height of the meniscus above the lower tip of the dilatometer was measured using the cathetometer, and the temperature was recorded. These measurements were checked after 10 minutes to ensure that temperature equilibrium had been attained. Raising or lowering the temperature enabled a second determination to be made with the other section of uniform capillary tubing.

Fig. 2.

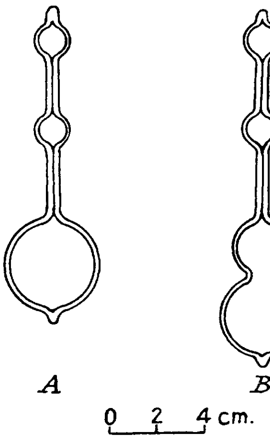
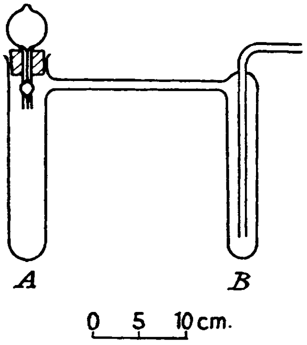


Fig. 3.



The dilatometer was dried, weighed, and then emptied using the apparatus shown in Fig. 3. The dilatometer was inserted into a rubber bung, and a scratch made at the centre of the upper measuring capillary. A sleeve of thin rubber tubing was placed over the scratch and the bulb of the dilatometer was cooled in solid carbon dioxide. The stem was broken under the sleeve, and the fragments of glass, which were retained inside the sleeve, were collected. The dilatometer was immediately inverted in the tube *A* (Fig. 3) which was cooled in solid carbon dioxide and, by means of a water-pump attached to trap *B*, the apparatus was evacuated. The bulk of the chlorine trifluoride was collected in *A*, and the remainder was condensed in trap *B* cooled in liquid air. The dilatometer was removed, rapidly rinsed with water, and then dried.

The dilatometer and glass fragments were weighed and the dilatometer was calibrated to the cut with distilled water at the temperature of the determination. The height of the cut above the tip of the dilatometer was measured with the dilatometer immersed in the thermostat, to minimise any errors due to distortion effects of the Dewar flask walls, and the bore of the capillary was measured by means of a thread of mercury. The volume of liquid chlorine trifluoride at the temperature of the determination could then be calculated. The volume of chlorine trifluoride at the lower temperature of determination was obtained in a similar manner. By a similar technique, the volume of chlorine trifluoride vapour over the liquid was determined and the weight of this vapour calculated as indicated previously.

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