The Determination of the Density of Liquid Bromine Pentafluoride.

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The density of liquid bromine pentafluoride has been determined over the range $-15°$ to $+76°$ in sealed Pyrex glass dilatometers. There was no attack on the glass. The results are expressed in the equation $d_4^t = 2{\cdot}5509 - 3{\cdot}484 \times 10^{-3}t - 3{\cdot}45 \times 10^{-6}t^2$.

Ruff and Menzel (*Z. anorg. Chem.*, 1931, **202**, 49) gave an equation representing the variation of the density of liquid bromine pentafluoride with temperature. Unfortunately they did not report the range of temperature covered or the estimated accuracy of their results. There is no other recorded measurement of the density of the liquid.

The present determinations were carried out over the range $-15°$ to $+76°$ essentially as described by Banks and Rudge (*J.*, 1950, 191) for liquid chlorine trifluoride.

In calculating the results, all weighings were reduced to vacuum; the weight of bromine pentafluoride present as vapour was calculated on the assumption that the vapour obeys the ideal gas laws and the pressure from the equation * $\log p = 8{\cdot}0716 - 1627{\cdot}7/T$ (Ruff and Menzel, *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 *

$$d_4^t = 2{\cdot}5509 - 3{\cdot}484 \times 10^{-3}t - 3{\cdot}45 \times 10^{-6}t^2$$

The experimental results, together with the values calculated from the above equation, are shown in Table 1. Table 2 gives calculated values of the density of bromine pentafluoride at regular temperature intervals and at the boiling point [40·5° (Ruff and Menzel, *loc. cit.*)].

The plot of $d = 2{\cdot}550 - 3{\cdot}46 \times 10^{-3}t$ (Ruff and Menzel, *loc. cit.*) crosses the curve of the present equation at $-20{\cdot}00°$ and $+13{\cdot}04°$. The divergence between the two equations is less than 0·1% from $-30°$ to $+30°$ and increases to 0·7% at 70°.

* In this paper T is the absolute temperature and t the temperature on the Centigrade scale.

TABLE 1.

Dilatometer No.	Temp.	d (obs.) (g./ml.)	d (calc.) (g./ml.)	$10^8(\Delta d)^2$ *	Dilatometer No.	Temp.	d (obs.) (g./ml.)	d (calc.) (g./ml.)	$10^8(\Delta d)^2$ *
6	−14·99°	2·6032	2·60235	72·2	3	40·80	2·4032	2·40301	3·6
5	− 4·29	2·5653	2·56579	24·0	2	42·94	2·3950	2·39494	0·4
1	+10·01	2·5150	2·51568	46·2	6	43·87	2·3916	2·39141	3·6
4	24·70	2·4621	2·46275	42·2	3	46·11	2·3832	2·38292	7·3
2	33·83	2·4290	2·42919	3·6	1	59·40	2·3319	2·33178	1·4
5	38·53	2·4120	2·41154	21·2	4	76·44	2·2639	2·26444	29·2

* $\Delta d = d$ (obs.) − d (calc.). The R.M.S. deviation of the calculated values from the observed values is 0·00046.

TABLE 2.

Temp....	−20°	−10°	0	+10°	20°	30°	40°	40·5°	50°	60°	70°	80°
d (calc.)	2·6192	2·5854	2·5509	2·5157	2·4798	2·4433	2·4060	2·4041	2·3681	2·3294	2·2901	2·2501

EXPERIMENTAL

Bromine pentfluoride was prepared from the elements in the vapour phase at 300° (Found : Br, 45·5; F, 55·3. Calc. for BrF_5 : Br, 45·7; F, 54·3%) and was freed from traces of hydrogen

FIG. 1.

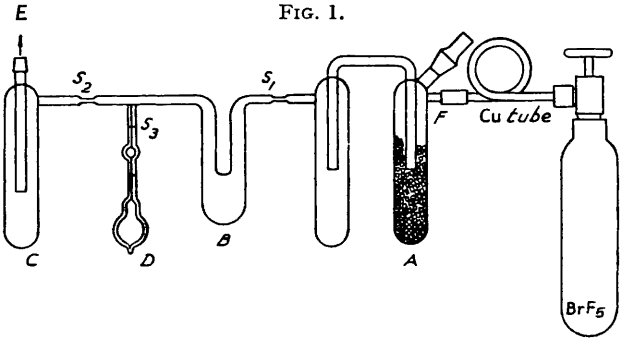
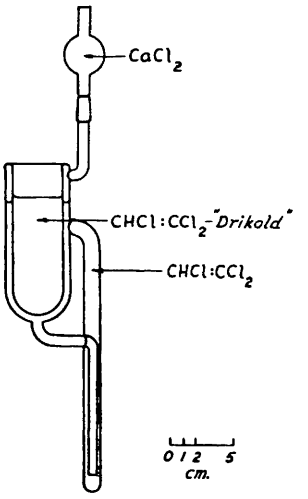


FIG. 2.



fluoride and bromine trifluoride by contact with sodium fluoride and further purified by distillation at reduced pressure.

A preliminary experiment designed to investigate the effect of bromine pentafluoride on glass was carried out to see whether there was any danger in sealing the liquid in glass dilatometers with very little free space. Weighed samples of Pyrex tube were sealed off *in vacuo* in ampoules containing sufficient bromine pentafluoride, purified by distillation through a tube packed with sodium fluoride pellets, to immerse half the specimen and were stored at room temperature for six days. The ampoules were then opened, the bromine pentafluoride was poured off and the samples were washed successively in wet carbon tetrachloride, dry carbon tetrachloride, and distilled water. They were reweighed after being dried at 140°. Samples of silica and of an experimental hydrogen fluoride-resistant glass (British Thomson-Houston Co. Ltd., Rugby) were also tested. All three types of glass showed weight losses not greater than 0·3 mg. for surface areas of 15—22 cm.^{2}.

The purification of this bromine pentafluoride was much less rigorous than that used during the dilatometer-filling operations and the method of destroying the film of bromine pentafluoride on the surface of the specimens probably led to a little attack by hydrogen fluoride. Even so, the overall effect on each of the samples was hardly measurable and it was considered

that more carefully purified bromine pentafluoride would be inert to Pyrex glass. The appearance of a trace of flocculent precipitate in the bromine pentafluoride in contact with the hydrogen fluoride-resistant glass sample indicated some slight reaction but there was no visible change in the contents of the remaining three ampoules.

Except for minor modifications, the technique used in the density determinations was essentially that described earlier (Banks and Rudge, *loc. cit.*) for the determination of the density of liquid chlorine trifluoride. Six dual-range dilatometers of 10 ml. capacity were used to obtain twelve results on six different samples of bromine pentafluoride.

The filling apparatus is shown in Fig. 1. Bromine pentafluoride vapour, led from a storage cylinder through a copper tube and Fyffe union *F*, was condensed *in vacuo* in trap *A* containing sodium fluoride pellets and cooled in solid carbon dioxide–trichloroethylene, dry air was admitted to the apparatus and, by removing the cooling bath from *A*, the solid pentafluoride was allowed to warm and melt. This procedure was repeated until sufficient bromine pentafluoride had been transferred. The liquid bromine pentafluoride, which at this stage had a very faint red colour, was allowed to remain in contact with the sodium fluoride for about half an hour and the apparatus was re-evacuated with trap *A* cooled in solid carbon dioxide. About 10% of the bromine pentafluoride was distilled into trap *C*, which was connected at *E* to the vacuum pump or dry air supply, cooled in liquid air until there was no trace of colour in the condensate. It is not known what impurity was responsible for this coloured fraction but in all cases the colour appeared only in the first fraction of the distillate. Trap *B* was then cooled in solid carbon dioxide–trichloroethylene, and bromine pentafluoride, in excess of that required to fill the dilatometer, was distilled into it. The dilatometer, *D*, and trap *B* were detached as a unit by sealing off *in vacuo* at the seals *S*1 and *S*2. The required amount of bromine pentfluoride was poured into the dilatometer and, after cooling both the dilatometer and the trap in liquid air, the dilatometer was sealed off at *S*3.

The Dewar flask with clear observation strips used as the thermostat for the work on chlorine trifluoride was used with minor modifications to give improved temperature control especially below room temperature. The thermosyphon cooling element shown in Fig. 2 was used, when required, to provide extra cooling and the thermostat temperature was controlled by electric heating as used for the higher temperatures. For reasons of safety, carbon tetrachloride was used rather than water as the bath liquid except during the measurement at 76° when trichloroethylene was used. To simplify the measurement of the position of the meniscus in the measurement capillaries, a calibration mark was etched at about the mid-point of each capillary and the temperature was adjusted to hold the meniscus steady for at least twenty min. on each of these marks in turn, the meniscus being observed through a telescope to eliminate parallax error. Temperatures were measured on a Beckmann thermometer graduated in 0·01° divisions which enabled minor fluctuations of temperature to be detected and controlled. The Beckmann thermometer was calibrated against mercury-in-glass thermometers calibrated by the N.P.L. to $\pm 0{\cdot}02°$. For the two measurements below 0°, the Beckmann thermometer was calibrated against a Chromel–Alumel thermocouple calibrated by the N.P.L. to $\pm 0{\cdot}1°$.

The dilatometers were emptied and calibrated with boiled-out distilled water by the method described previously except that for speed and simplicity the calibrations were carried out at 50° for the higher range of each dilatometer and 25° for the lower range. Two dilatometers were recalibrated to the lower mark at 75° and the results were used to determine the coefficient of expansion of the glass ($1{\cdot}0 \times 10^{-5}$, $1{\cdot}2 \times 10^{-5}$). The volume of each dilatometer at the experimental temperature was then calculated. Visual examination of the dry dilatometers, after calibration, revealed no evidence of etching.

From a consideration of the individual experimental errors involved, the expected measurement errors in the density values obtained are within $\pm 0{\cdot}0003$ g./ml. for ten of the results and $\pm 0{\cdot}0006$ g./ml. for the two results at temperatures below 0°.

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