CCCXCVI.—*The Critical Temperatures of Boron Trichloride and Silicon Tetrachloride.*

By Thomas Wallace Parker and Percy Lucock Robinson.

An investigation involving the determination of critical temperatures is in progress in this laboratory, and these results are submitted because no previous determination appears to have been made in

the case of boron trichloride, whilst the only one relating to silicon tetrachloride is that of Mendeléev (*Annalen*, 1861, **119**, 11). Carefully purified material has been used in each case, and the thermometers have been standardised at or very near to the readings actually used by the National Physical Laboratory, so that considerable trust may be placed in these values.

EXPERIMENTAL.

Preparation of Materials and Filling of Tubes.—The Durosil glass-ware used in these operations was cleaned by treatment with chromic–nitric acid mixture, well washed with numerous changes of water, the last portions being good distilled water, and with alcohol and ether, after which it was dried by heating to 110° in an electric oven.

Boron trichloride. About 120 c.c. of boron trichloride, which had been used for an approximate determination of density (see Briscoe, Robinson, and Smith, this vol., p. 284) and had remained sealed under vacuum in a container provided with a special joint, constituted the initial material for this work. This liquid was subjected to two successive fractional distillations in a vacuum, head and tail fractions of about 5 and 10 c.c. respectively being rejected on each occasion, and the main fractions being received into vessels having special joints. The fractionations were performed with the usual precautions taken in this laboratory and described elsewhere for ensuring the absence of leaks in the train, of moisture on the interior surface of the vessels, and of residual air. The vessel, L, containing the main fraction (90 c.c.) was now attached to the train illustrated in Fig. 1; B_1—B_8 represent the various critical-temperature tubes, with walls 1 mm. thick and bore 4—5 mm., and provided with the thickened capillaries necessary for sealing off under a vacuum; M is the surface-tension vessel previously described (Mills and Robinson, this vol., p. 1823); and N is a vessel with a special joint for receiving the surplus material. This train was evacuated and slowly refilled with dry air 6 times while at 150°, to ensure careful drying, and was sealed off from the pump under the highest vacuum attainable. The special joint was then broken, and the liquid was distilled, solid carbon dioxide–ether being used as refrigerant, into tubes B_1, B_2, and B_3; M was then filled to the requisite level and removed; next, B_4, B_5, B_6, and B_7 were filled and removed in the order indicated, and, the major portion of the residual liquid having been distilled into N, which was drawn off, B_8 was filled and removed. The normal procedure in charging the critical-temperature tubes was

to fill them with liquid and then distil back to the main bulk until the desired quantity remained in the tube, the final sealing being done without arrest in the backward flow of vapour. It could thus be reasonably presumed that the tubes contained only the slightest trace of air, if any at all.

Silicon tetrachloride. The material used was the head fraction of silicon tetrachloride obtained from the second vacuum distillation of the U.S.A. sample (see Robinson and Smith, J., 1926, 1272) and was considered of sufficient purity for immediate use. A train

FIG. 1.

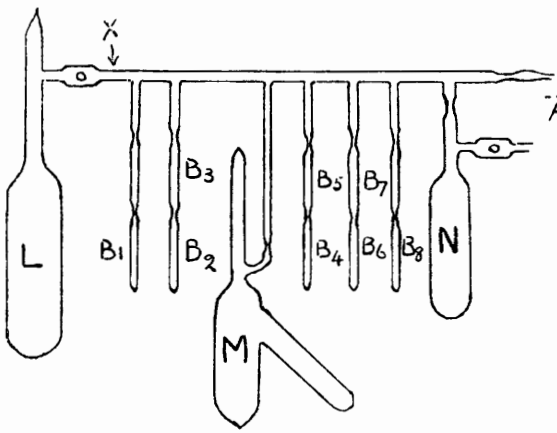
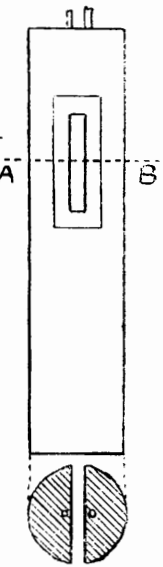


FIG. 2.



Elevation and Section through AB.

similar to Fig. 1 was employed. A head fraction of 2 c.c. was first taken in N, tubes B_1, B_2, B_3, and B_4 were successively filled and removed, and then M was filled. As described elsewhere (Mills and Robinson, *loc. cit.*), when M had received sufficient liquid a fracture occurred in the special joint of L and this vessel was at once drawn off at X, the apparatus was immediately attached to the pump at B_8, rapidly evacuated, and sealed off above this point, after which M was removed. This unfortunate accident rendered it impossible to fill further tubes.

Critical-temperature Apparatus and Phenomena.—Apparatus. This was a modification of that of Hackspill and Mathieu (*Bull. Soc. chim.*,

1919, **25**, 482). A cylinder of copper (Fig. 2), 5 cm. × 27 cm., with a central hole 11 mm. in diameter and two other holes 7 mm. in diameter and reaching almost to the bottom, was constructed for us in the Department of Engineering by the courtesy of Prof. C. J. Hawkes. The metal between the outer and the central holes was 2 mm. at the thinnest parts. A window, 4 cm. high and the width of the central hole, was cut completely through the metal about 10 cm. from the top. This window was closed by thick sheets of colourless mica, bound in position by means of copper wire. The critical-temperature tube was placed in the central hole, and rested on a length of glass rod at a height convenient for observation. The thermometers were similarly supported in the side holes, so that the bulbs were level with the middle of the critical-temperature tube, correction for exposed stem being made when necessary. The apparatus with the tube and thermometers in position was placed inside a heater (kindly lent to the authors by Dr. L. A. Sayce) consisting of a sheet-copper cylinder 22 in. × 6 in., fitted on opposite sides with vertical glass windows 1 in. wide, and heated by a spiral winding of nichrome wire insulated from the copper by a layer of asbestos board. The bottom was well lagged and a lid of several thicknesses of asbestos board closed the top. This arrangement, used with suitable external resistances, was found to change the temperature of the metal cylinder very slowly and uniformly, while tests made by changing the thermometers from hole to hole showed that under the conditions prevailing during the experiments, a difference in temperature of less than $\pm$ 0·1° was to be expected in the three positions.

Phenomena. Young (*Phil. Mag.*, 1906, **20**, 803) and Travers and Usher (*Proc. Roy. Soc.*, 1906, **78**, 247) seem to have found the phenomena attending the change of state susceptible of much sharper observation than did Hackspill and Mathieu (*loc. cit.*), who state that it is difficult to observe the critical phenomena to less than $\pm$ 1·0°. The present authors, in common with most observers, have taken the temperature recorded at the appearance of the meniscus in the cloud during the change from vapour to liquid as the critical temperature. This phenomenon was observed against a bright background, and as there was an easily perceptible change during a fall of 0·2°, it is probable that the individual readings for identical conditions of the cloud were within $\pm$ 0·1° of the actual temperature. This is probably much beyond the constancy to be expected in the temperature at which identical appearances occur in separate experiments. Tubes filled to the extent of one-third of their volume gave the most satisfactory critical phenomena. The results are in the table.

Liquid.	Tube.	Successive observations at same heating.						Mean.
BCl_3	B_2	178·8°	178·7°	178·7°				178·7°
	B_4	178·9	178·9	178·8				178·9
	B_6	178·7	178·7	178·7				178·7
	B_6	178·9	178·8	178·7				178·8
$SiCl_4$	C_2	233·5	233·5					233·5
	C_3	233·6	233·5	233·5				233·5
	C_4	233·9	233·8	233·8	233·6°	233·6°	233·5°	233·7

The results for boron trichloride do not indicate any real difference from tube to tube, and give a mean value 178·8° ± 0·2°, but they do show that there is a tendency for the value to fall if the material is maintained at or about the critical temperature for some time. Two days before the determinations for B_2 given above, the tube was accidentally heated to 210° and then gave two successive results of 178·4°. There is some reason to suppose that the regular differences in the critical temperature observed in successive heatings, although not much greater than the probable experimental error, may in fact be real. If so, it appears that heating the liquid to a higher temperature causes a depression of the critical temperature which may be due to a change in the physical properties of the liquid, but which, in the opinion of the authors, is not caused, in the case of a compound such as boron trichloride, by thermal dissociation. Similar differences are shown in the case of silicon tetrachloride, particularly in tube C_4. The mean value of the critical temperature is 233·6° ± 0·2°, which is rather higher than that due to Mendeléev (*loc. cit.*).

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
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