

### 604. *The Electrical Conductivity of Chlorine Trifluoride, Bromine Trifluoride, and Iodine Pentafluoride.*

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The specific conductivities of chlorine trifluoride, bromine trifluoride, and iodine pentafluoride are  $<10^{-6}$  (at 0°),  $8.0 \times 10^{-3}$  (at 25°) and  $2-3 \times 10^{-5}$  (at 25°)  $\text{ohm}^{-1}\text{cm}^{-1}$ , respectively. That of bromine trifluoride decreases with temperature in the range 15–60°, but for iodine pentafluoride there is a positive temperature coefficient. Ohm's law is obeyed in the case of bromine trifluoride but not in that of iodine pentafluoride. The existence of the ions  $\text{BrF}_2^+$  and  $\text{BrF}_4^-$  in liquid bromine trifluoride is postulated to explain the observed phenomena.

THE main interest in conductivity measurements on the interhalogen compounds lies in their bearing on structural problems, and in general the ability to form ions should be related to the different electronegativities of the halogens. No observations on the electrical conductivities of the halogen fluorides have been reported, although iodine monochloride, monobromide, and trichloride have been studied both in the liquid state and in solution. The specific conductivity of iodine monochloride is variously given as  $4.6 \times 10^{-3}$  (Cornog and Karges, *J. Amer. Chem. Soc.*, 1932, **54**, 1886),  $5.1 \times 10^{-3}$  and  $4.52 \times 10^{-3}$   $\text{ohm}^{-1}\text{cm}^{-1}$  (Fialkov, *J. Gen. Chem. Russia*, 1941, **11**, 910; 1948, **18**, 14). Walden (*Z. physikal. Chem.*, 1903, **43**, 385) has studied solutions of this substance in arsenic trichloride and sulphur dioxide. The values published for iodine monobromide at 40° are  $3 \times 10^{-4}$  (Bruner and Beckier, *Z. Elektrochem.*, 1912, **18**, 368) and  $6.4 \times 10^{-4}$   $\text{ohm}^{-1}\text{cm}^{-1}$ . Compared with the higher values for the monochloride, these seem to show the effect of the difference in electronegativity of the halogens. Measurements on solutions of the monobromide in sulphur dioxide, bromine, and nitrobenzene have also been made (Walden, *loc. cit.*; Finkelstein, *Z. physikal. Chem.*, 1925, **115**, 303). Solutions of iodine trichloride have been studied (Walden, *loc. cit.*; Finkelstein, *loc. cit.*; Plotnikov, *Chem. and Ind.*, 1923, **42**, 750; Bruns, *Z. physikal. Chem.*, 1925, **118**, 89; Birr, *ibid.*, 1933, **165**, A, 311) and preliminary investigations (N. Greenwood, unpublished observations in this laboratory) indicate that fused iodine trichloride has a conductivity of the same order as bromine trifluoride, referred to below.

The halogen fluorides are much more reactive than the iodine chlorides and the bromide, and physicochemical measurements are correspondingly more susceptible to errors due to impurities. Chlorine trifluoride, the most reactive of the three substances examined, has, however, a negligible conductivity. This shows its covalent character and is consistent with the comparatively low boiling point (11.3°) and the non-formation by it of polyhalide ions (Sharpe and Emeléus, *J.*, 1948, 2135). Bromine trifluoride, the boiling point of which is 127°, has a specific conductivity at 15° of  $8.1 \times 10^{-3}$   $\text{ohm}^{-1}\text{cm}^{-1}$ , which decreases as the temperature increases from 15° to 60°. This value is similar to that for iodine monochloride and it is noteworthy that both compounds have high Trouton constants, in common with associated liquids ( $\text{BrF}_3$ , 25.3;  $\text{ICl}$ , 27;  $\text{H}_2\text{O}$ , 25.9). A negative temperature coefficient may be associated with electronic conduction, but this type of current transfer is unlikely in bromine trifluoride since the conductivity of the solid is roughly one thousandth of that of the liquid, whereas in true electronic conduction this difference would be very much less pronounced (von Hevesy, *Kgl. Danske Videnskab. Medd.*, 1921, III, Nr. 13, 1). The conduction is more readily explained by postulating the existence in liquid bromine trifluoride of the ions  $\text{BrF}_2^+$  and  $\text{BrF}_4^-$ , the negative temperature effect being then due to a decrease in the stability of one or both of these ionic species with increasing temperature. The great reactivity of the trifluoride precludes a study of the conductivity in most solvents and it would be difficult to characterise these ions in solution. Indirect evidence of the existence of the  $\text{BrF}_4^-$  anion is provided, however, by the isolation of the compounds  $\text{KBrF}_4$ ,  $\text{AgBrF}_4$ , and  $\text{BaBr}_2\text{F}_8$  (Sharpe and Emeléus, *loc. cit.*) similar in type to the analogous ionic compound  $\text{KICl}_4$  derived from iodine trichloride. The fact that bromine trifluoride conducts in the solid state although the conductivity is much less than in the liquid

state suggests that the solid may have an ionic lattice. This is all the more probable since phosphorus pentachloride, which conducts to a very small extent in the solid, has been shown to possess a lattice of  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$  ions (Clark, Powell, and Wells, *J.*, 1942, 642).

Iodine pentafluoride, the specific conductivity of which is  $2-3 \times 10^{-5}$  at  $25^\circ$  and which has a positive temperature coefficient, must also contain ions in the liquid, though the evidence as to their nature is less convincing. Since the compound  $\text{KIF}_6$  has been isolated (Emeléus and Sharpe, this vol., p. 2206) it is possible that they are  $\text{IF}_4^+$  and  $\text{IF}_6^-$ , the increase in conductivity with temperature being due to the increasing mobility of the ions more than compensating for their thermal instability. Bromine trifluoride and iodine pentafluoride differ further in that direct-current measurements show the former to obey Ohm's law whereas the latter does not. The cation  $\text{BrF}_2^+$  would be expected on discharge to give bromine trifluoride and bromine monofluoride (brown), whereas the  $\text{BrF}_4^-$  anion should give bromine trifluoride and pentafluoride (colourless). During prolonged electrolysis there is no gas evolution but the cathode liquid becomes brown and is separated by a sharp boundary from the rest of the liquid in the cell, which remains a clear yellow (see below). At this boundary it is probable that reaction occurs between the pentafluoride and monofluoride, with formation of the trifluoride. This phenomenon may explain in part the absence of measurable polarisation effects at the electrodes, and the consequent validity of Ohm's law, since the mutual interaction of the electrolysis products as they diffuse away from the electrodes, and the fact that they re-form the solvent, would tend to keep their concentrations round the electrodes to a low value and so minimize polarisation effects. Other factors, however, are also involved in determining the electrode phenomena and there is as yet no experimental basis for a discussion of the absence of a decomposition potential in bromine trifluoride. Iodine monochloride and trichloride also obey Ohm's law when subjected to a direct-current voltage. In the case of iodine pentafluoride there is direct evidence of a concentration polarisation effect, and this may arise from the lower diffusion rate of the products formed at the electrodes or from their less ready interaction to re-form iodine pentafluoride.

#### EXPERIMENTAL.

*Preparation of the Interhalogen Compounds.*—Chlorine trifluoride was prepared by leading streams of chlorine and fluorine (21.4 and 13.3 g./hr., respectively) through a packed reactor at  $280^\circ$ . The reactor was a flanged nickel tube (2" internal diam., 12" long) fitted at one end with inlet tubes for the two gases and at the other with an exit tube and a 6" long thermometer pocket. The tube was packed with silver-plated copper chips. Chlorine trifluoride collected as a pale yellow liquid in a quartz trap at  $-78^\circ$  and was purified by passing the vapour through a metal tube packed with sodium fluoride pellets to remove hydrogen fluoride, and by a series of trap-to-trap fractional condensations in vacuum, using quartz apparatus, immediately before filling the conductivity cell.

Bromine trifluoride was prepared from the elements (Sharpe and Emeléus, *J.*, 1948, 2135) and purified by distillation at atmospheric pressure in a steel apparatus, the fraction boiling at  $126-128^\circ$  being collected. This was further purified before use by redistilling it under reduced pressure at room temperature in an all-quartz apparatus. All the possible impurities, bromine, hydrogen fluoride, bromine monofluoride (b. p. ca.  $20^\circ$ ), and bromine pentafluoride (b. p.  $40.5^\circ$ ) were more volatile than the trifluoride, and the change in colour of the liquid from orange to light yellow, due to the removal of the least volatile impurity, bromine, afforded a convenient visual indication of when to begin collecting the pure trifluoride. In the final purification the liquid was distilled in vacuum into the conductivity cell.

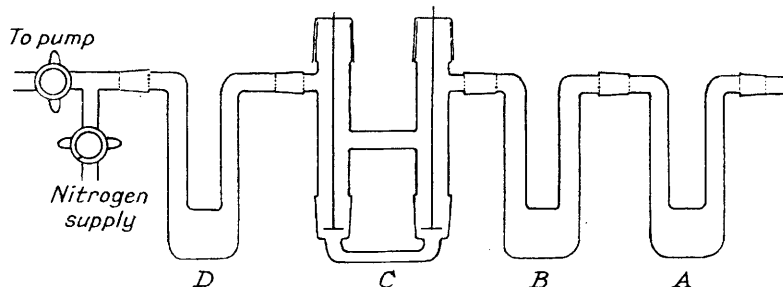
Iodine pentafluoride was prepared similarly by the direct fluorination of resublimed iodine in a water-cooled silica trap which was shaken mechanically. The passage of fluorine was stopped when the product became colourless. The liquid was distilled immediately before use after traces of iodine formed by decomposition had been removed by further passage of fluorine (Found: I, 57.0; F, 42.2. Calc. for  $\text{IF}_5$ : I, 57.2; F, 42.8%).

*Conductivity Measurements.*—The measurements with chlorine trifluoride and a number of the earlier measurements with bromine trifluoride and iodine pentafluoride were made with a standard Wheatstone bridge circuit, a telephone detector being used to determine the point of balance. At a later stage a cathode-ray oscillograph was used as a null-point detector, the circuit being based on that described by Lawson (*Rev. Sci. Instr.*, 1938, 9, 272). Conductivity cells for use with chlorine and bromine trifluorides were made of quartz, which resists attack by these compounds. Iodine pentafluoride was found to expand when it melted and to fracture the silica cell. In this case, and also because of the lower reactivity of the compound, cells made of Pyrex glass were used in most of the experiments. The final design of the silica cell is shown in Fig. 1. Circular platinum electrodes (30 S.W.G.) of 1.5-cm. diam. were rivetted to 2-mm. diam. platinum rods and held in B.24 copper cones. The internal diameter of the vertical limbs of the cell was 1.8 cm. It was charged with about 10 c.c. of liquid, the resistance being independent of the height of the liquid and of rotation of the electrodes provided the discs were covered.

Two types of cell of a more conventional type were used with iodine pentafluoride. The first [Fig. 2(a)] was made of Pyrex glass with sealed-in platinum electrodes about 0.5 cm. apart and mercury contacts in the side arms. There was a tendency to leakage at the platinum seals. The second type, also made of Pyrex glass, had circular nickel electrodes; the connections were led in through glass-metal unions which were above the liquid level [Fig. 2(b)]. A reservoir attached to the side of the cell was used in adjusting the liquid level and also for preparing solutions of salts in iodine pentafluoride.

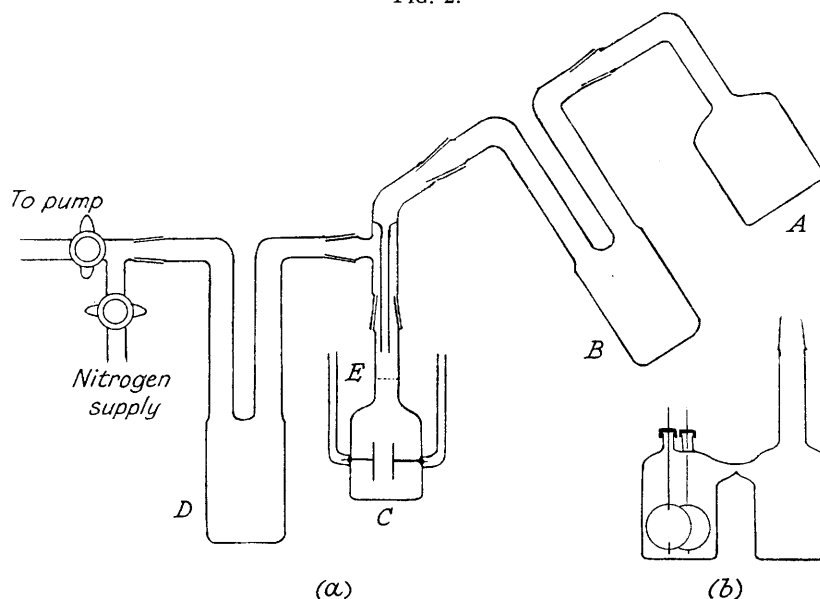
The apparatus used in filling the cell with chlorine or bromine trifluoride is shown in Fig. 1. The quartz traps, *A*, *B*, and *D*, and the cell, *C*, connected by B.14 joints, were assembled as shown and the apparatus was evacuated and flamed. In filling the cell with chlorine trifluoride a sufficient quantity was distilled in vacuum from a quartz storage vessel into *A*. This vessel was removed under a positive

FIG. 1.



pressure of dry nitrogen and the open end of *A* was closed. The contents of *A* were then distilled slowly in vacuum through *B* (at  $-120^{\circ}$ ) into *D*, which was cooled in liquid nitrogen. Chlorine trifluoride condensed in *B*, any more volatile impurities passing into *D*. About 10 c.c. of liquid were then distilled in vacuum from *B* into *C*, dry nitrogen was admitted and the cell was disconnected. Its open ends were protected from moisture by sodium fluoride-silica gel drying tubes.

FIG. 2.



In the case of bromine trifluoride about 15 c.c. of the freshly distilled liquid were poured into *A* and frozen in liquid air, the apparatus being then evacuated. About 2 c.c. of liquid were distilled from *A* into *D* to remove volatile impurities, *B* was cooled in liquid nitrogen and the greater part of the bromine trifluoride distilled from *A* to *B*. A small residue of ferric fluoride, formed by attack on the steel storage bottle, remained in *A* together with any other non-volatile impurities. Finally *C* was cooled and about 10 c.c. of liquid were distilled from *B* into it. In some experiments dry nitrogen was admitted to the system and the cell remained attached to the vacuum line, conductivity measurements being made with *D* and *B* immersed in liquid nitrogen and *C* in a constant-temperature bath. In other cases the cell was removed as in the work with chlorine trifluoride, and its ends closed by guard tubes to exclude moisture.

The above procedure was modified for iodine pentafluoride to allow the liquid to be poured into the cell [*C*, Fig. 2(a)], the capacity of which was about 40 c.c. 50 c.c. of iodine pentafluoride were poured into *A* and 10 c.c. were distilled at 6–8 mm. into *D* to remove volatile impurities. At lower pressures the liquid in *A* solidified and distillation was very slow. The residue in *A* was then distilled into *B*, the apparatus was filled with dry nitrogen, and, by rotating *B* through  $180^{\circ}$ , its contents were transferred to the cell so as to fill it to the marked level *E*. The cell was detached under a positive nitrogen pressure,

stopped, and immersed in a thermostat for conductivity measurements. In most cases stopcocks and joints were carefully lubricated with a silicone grease, the fluorocarbon lubricants available being too thin for satisfactory working. A mixture of a fluorocarbon with the silicone grease was necessary for the iodine pentafluoride distillation. It was essential to avoid contact of any grease with the liquid halogen fluorides.

Measurements with chlorine trifluoride were made at 0°. For each of a series of samples purified as already described the cell resistance was found to be infinite with the apparatus used, showing that the conductivity was less than  $10^{-6}\text{ohm}^{-1}\text{cm}^{-1}$ . With bromine trifluoride a large number of preliminary experiments indicated a specific conductivity of the order of  $8 \times 10^{-3}\text{ohm}^{-1}\text{cm}^{-1}$ . In view of the great reactivity of this substance it was thought that this result might be due to impurities formed by attack on the cell or the electrodes or formed by reaction with traces of moisture. The conductivity changed little with time, however, as is shown by the fact that at  $25.00^\circ \pm 0.02^\circ$  after 67 hours the value had risen from  $8.00 \times 10^{-3}$  to  $8.37 \times 10^{-3}\text{ohm}^{-1}\text{cm}^{-1}$ . In this experiment the cell was detached from the vacuum apparatus and fitted with guard tubes. When the cell was attached to the vacuum system with liquid-air traps on either side a variation of resistance could not be detected in 3 hours and was 1% in 6 hours. The addition of free bromine decreased the conductivity, as is shown by the following data :

Wt. (g.) of Br added to 27.9 g. of $\text{BrF}_3$ .....	0	1.07	2.93	3.82
Time (mins.) .....	0	165	200	335
Conductivity ( $\text{ohm}^{-1}\text{cm}^{-1} \times 10^3$ ) at $25^\circ$ .....	8.00	7.02	7.00	7.72

Measurements of the variation of conductivity with temperature made on two carefully purified samples of bromine trifluoride (A and B) gave the following results :

Temperature .....	$10.1^\circ$	$14.8^\circ$	$25.0^\circ$	$35.0^\circ$	$45.0^\circ$	$55.0^\circ$
Conductivity, $\text{ohm}^{-1}\text{cm}^{-1} \times 10^{-3}$ (A) .....	8.12	8.11	8.00	7.78	7.48	7.08
Temperature .....	$9.0^\circ$	$10.0^\circ$	$20.0^\circ$	$30.0^\circ$	$40.0^\circ$	$60.0^\circ$
Conductivity, $\text{ohm}^{-1}\text{cm}^{-1} \times 10^{-3}$ (B) .....	8.13	8.14	8.09	7.87	7.58	6.75

After sample B had been heated in the cell to  $60^\circ$  the value at  $20^\circ$  was redetermined and found to be unaltered. There was little variation of conductivity with temperature below  $20^\circ$ , and in one experiment a sample supercooled  $4.4^\circ$  below the m. p. ( $8.8^\circ$ ) had a conductivity of  $8.12 \times 10^{-3}\text{ohm}^{-1}\text{cm}^{-1}$ . On solidification, however, the conductivity was greatly diminished. Measurements on the solid are unlikely to be accurate because of the possibility of imperfect contact with the electrodes. The following data show, however, that in this range there is a positive temperature coefficient :

Temperature .....	$4.0^\circ$	$5.0^\circ$	$6.0^\circ$	$7.3^\circ$	$8.0^\circ$
Conductivity, $\text{ohm}^{-1}\text{cm}^{-1} \times 10^{-5}$ .....	2.3(6)	2.6(0)	3.9(0)	7.8(0)	17.3(5)

Ohm's law was found to be obeyed when a direct-current voltage was applied to a cell containing bromine trifluoride. A normal potentiometer circuit was used in these measurements, the following being typical measurements made at  $25^\circ$  :

Voltage .....	0.0336	0.0664	0.098	0.144	0.177	0.212	0.266
Current $\times 10^6$ .....	30	60	90	130	160	190	240
$10^{-3} V/C$ .....	1.12	1.11	1.09	1.11	1.11	1.12	1.11
Voltage .....	0.306	0.394	0.518	0.620	0.702	0.810	0.875
Current $\times 10^6$ .....	280	360	480	560	640	740	800
$10^{-3} V/C$ .....	1.09	1.09	1.08	1.11	1.10	1.10	1.09

Similar results were obtained with solid bromine trifluoride at  $0^\circ$ , the current being of the order of  $10^{-3}$  of that passing through the liquid. The resistance of the cell calculated from these measurements agreed with the value using alternating current. When a potential of 25 volts was applied to the trifluoride at  $25^\circ$  for 1 hour, no gas was evolved but the liquid in the cathode limb became brown whereas that in the anode limb remained yellow. There was a permanent sharp colour boundary about midway along the connecting U-tube.

Measurements of the conductivity of iodine pentafluoride were less reproducible than those for bromine trifluoride, but a value of the order of  $10^{-6}\text{ohm}^{-1}\text{cm}^{-1}$  was obtained. The following are typical values obtained on two samples :

Temperature .....	$10.0^\circ$	$15.0^\circ$	$20.0^\circ$	$25.0^\circ$	$31.0^\circ$	$39.0^\circ$	$40.0^\circ$
Conductivity, $\text{ohm}^{-1}\text{cm}^{-1} \times 10^{-5}$ (A) .....	1.61	1.89	2.08	2.30	2.52	2.78	2.81
Temperature .....	$9.8^\circ$	$25.0^\circ$	$35.0^\circ$	$10.2^\circ$ (C)	$13.5^\circ$ (C)	$19.0^\circ$ (C)	$25.0^\circ$ (C)
Conductivity, $\text{ohm}^{-1}\text{cm}^{-1} \times 10^{-5}$ (B & C) .....	1.78	2.45	3.12	1.91	2.05	2.28	2.55

Measurements for A and B were made with platinum electrodes, but for C, electrodes of nickel were used. Specific conductivities at  $25^\circ$  as high as  $5-6 \times 10^{-5}\text{ohm}^{-1}\text{cm}^{-1}$  were obtained with iodine pentafluoride which had been less rigorously purified. The results show that, in contrast to bromine trifluoride, there is a positive temperature coefficient. Addition of iodine increased the conductivity, though its solubility was apparently very limited. Thus when 0.1 g. of iodine was added to approximately 40 c.c. of the pentafluoride at  $25^\circ$  the resistance fell from 2296 to 2000 ohms. The solution was dark brown but the iodine had not dissolved completely.

Direct-current measurements with pure iodine pentafluoride show that Ohm's law was not obeyed.

The following are typical results, though in this case the reproducibility was poor. The value of the current passed depended on time, indicating a concentration polarisation effect.

Voltage .....	0.10	0.60	1.00	2.00	3.00	5.00
Initial current .....	0.01	0.18	0.31	0.60	1.07	1.83
Current after 120 secs. ....	—	0.07	0.15	0.43	0.82	1.51

When the current passing through the cell at a given voltage became practically constant, the applied potential was removed and the current produced by the cell acting as its own source of e.m.f. was measured by reversing the galvanometer leads. The following are typical results for an initial applied voltage of 0.5 volt.

Current produced by 0.5 volt (microamps.) .....	100	85	80	75	70	65	61	57	55	54
Time (secs.) .....	10	20	30	40	60	90	120	180	240	300
Current produced by cell .....	-50	-26	-19	-14	-11	-9	-5	-3	-1	
Time (secs.) .....	310	320	330	340	350	360	420	480	540	

With higher voltages free iodine was formed at the cathode and settled in the bottom of the cell.

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