

XXXV.—*Some Reactions and New Compounds of Fluorine.*

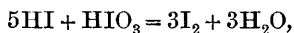
By EDMUND BRYDGES RUDHALL PRIDEAUX, M.A., B.Sc.

PART I. *Preparation of the Fluorine and Halogen Fluorides.*

THE electrolysis of hydrogen fluoride was carried out according to the well-known procedure due to Moissan. Some modifications related chiefly to details of manipulation and do not call for mention here. It is, however, a noteworthy fact that fluorine thus produced contains, even after prolonged electrolysis, an appreciable amount of oxygen. The presence of oxygen, clearly proved by two experiments especially designed for the purpose, should be taken into account by future investigators, since oxygen generated under such conditions necessarily contains ozone. Now many of the substances which combine easily with fluorine are also acted on to some extent by ozone, whilst the instability of ozone and our scanty knowledge of its physical constants render it a most undesirable impurity of fluorine required for physicochemical investigations. The ozone must therefore be converted into oxygen, and the conversion was effected by heating a section of the metal tubes through which the gases passed before being used. The apparatus has already been described by Mr. Cuthbertson and the author (*Phil. Trans.*, 1905, Series A, 205, 325).

Iodine Fluoride.

Fruitless attempts were made to prepare a higher fluoride of iodine. The result was in every case the characteristic colourless pentafluoride described by Moissan (*Compt. rend.*, 1902, 135, 563), who published the result of two analyses carried out by a gravimetric method. In the present instance, many analyses were carried out by an entirely different, volumetric method, and the results are worth recording both on this account and because of the rarity of the compound. The volumetric method proved rapid and convenient and was briefly as follows. The tube containing the colourless fluoride was sealed and plunged into standard alkali, the excess of which was afterwards found by titration. The solution was then made decidedly acid and solution of potassium iodide was added. The iodine liberated according to the equation :



was then titrated in the usual way. One-sixth of the iodine thus found was calculated as cubic centimetres of normal acid and subtracted

from the total amount of normal acid equivalent to the compound IF_5 . This had been determined by titration. The difference gives the standard acid equivalent to the fluorine and hence the weight of fluorine in the compound.

The results are tabulated below.

Iodine.	Fluorine.	Iodine fluoride.	$\frac{\text{I} \times 100}{\text{IF}_5}$.	$\left\{ \begin{array}{l} \text{Iodine found was confirmed} \\ \text{by } \text{AgIO}_3 \longrightarrow \text{AgI from} \\ \text{an aliquot part of the} \\ \text{solution.} \end{array} \right.$
0.112	0.080	0.192	58.11	
0.2195	0.1485	0.368	59.1	
0.077	0.0564	0.1334	57.7	
0.0365	0.028	0.0645	56.6	

Mean percentage of iodine = 57.9.
 IF_5 requires = 57.2.

The specific gravity of the compound roughly determined gave values the average of which is 3.5.

Moissan (*loc. cit.*) has not confirmed the observation of McIvor (*Chem. News*, 1875, 22, 229) that the pentafluoride is violently acted on by water with a hissing sound and great development of heat. This difference of opinion is probably attributable to different conditions. The former experimenter poured some pentafluoride into water and observed only a slight warming, while the latter presumably allowed the water to come into contact first with an excess of the substance with the effect mentioned above.

Liquid Fluorine and Iodine.—A fractionating bulb containing iodine was immersed in liquid air and fluorine was then liquefied in the same bulb. There is no chemical action; the pale yellow liquid fluorine also dissolves no iodine, since it may be distilled into another bulb and back again without altering in appearance. When the tube is sealed off and removed from the liquid air, a dark colour soon appears in the layer of fluorine next to the iodine, the whole rapidly liquefies, and an energetic action sets in with projection of white fumes some way up the tube; finally, a pale green flame appears for a few seconds.

Bromine Fluoride.

The fact that fluorine acts on bromine with the formation of some definite fluoride has been put on record by Moissan (*Le Fluor et Ses Composes*, p. 123). As, however, the study of halogen fluorides seemed to have been abandoned since his note on iodine pentafluoride, IF_5 (1902), it seemed desirable to fill this gap in our knowledge. A compound was prepared by the action of fluorine on bromine and analysed for the first time. The formula of the new compound and some of its

properties have been published in a brief note to the Chemical Society (*Proc.*, 1906, 22, 19). The following is a more detailed account of the results attained. The formula has since been confirmed by an independent research of M. Lebeau (*Compt. rend.*, 1905, 141, 1015), who has described additional properties of this interesting compound.

Comparison of Halogen Fluorides.—A study of the relations between iodine and fluorine leads to the conclusion that the only fluoride which gives concordant results on analysis is that which exists when the change of appearance and properties has become complete and shows a definite end-point. Further, it was found that this compound would combine with no more fluorine and was therefore the highest fluoride. A similarity was to be expected in the relations between bromine and fluorine. Experiment showed that there was indeed a general similarity, but that the two reactions differed in one respect. Iodine liquefies almost immediately, forming a homogeneous dark liquid which, on further passage of fluorine, separates only incompletely into an upper colourless and lower dark layer. On the other hand, the surface of bromine is at once covered by a distinct layer, having the appearance of the saturated fluoride, and this layer grows at the expense of the bromine, the line of demarcation remaining until all the bromine has disappeared. This seems to point to a probability that no fluoride of bromine can exist containing less than three atoms of fluorine to one of bromine. The non-existence of a higher fluoride was proved by experiments in which a large excess of fluorine was passed over the compound, which is therefore probably the only compound of fluorine with bromine. Liquid fluorine behaves in the same way towards solid bromine as it does towards iodine. The liquid remains of a pale yellow colour and when allowed to boil off the solid bromine there is no difference of appearance between the first fraction and the last.

Several attempts were made to determine the composition by the volumetric method described above in the case of iodine pentafluoride. Bromine was in this case set free on merely acidifying the alkaline solution and it soon became evident from this and other considerations that the fluoride in question was not BrF_5 . The following method of analysis was therefore adopted. The tube containing the compound was broken under standard alkali. The solution having the appearance and smell of hypobromite was warmed to decompose this into bromate and bromide. It was then neutralised with standard nitric acid.

The bromine, being present partly as bromate and partly as bromide, was estimated by a method recently described. Jannasch and Jahn (*Ber.*, 1905, 38, 1576) state that bromates are completely reduced to

bromides when heated with excess of fuming nitric acid. The bromine obtained in this manner from a known mixture of bromide and bromate was within one per cent. of the theoretical value.

To the solution prepared as above was added a little sodium carbonate and excess of pure calcium nitrate, the calcium fluoride being weighed as usual. The filtrate was concentrated by evaporation and treated with excess of silver nitrate and nitric acid. The silver bromide was filtered off, the process repeated with the filtrate, and the whole of the silver bromide dried and heated to constant weight.

The mean of two experiments carried out in this way gave :

$$\left. \begin{array}{l} \text{Br} = 57.5 \quad \text{Theoretical} \\ \text{F} = 42.5 \quad \text{for BrF}_3 \end{array} \right\} \begin{array}{l} \text{Br} = 58.4. \\ \text{F} = 41.6. \end{array}$$

It was mentioned above that the excess of alkali used for decomposing the bromine trifluoride was titrated with standard nitric acid. The result furnishes a useful check on the gravimetric values, for the latter give the weight of bromine and fluorine, which may of course be expressed as cubic centimetres of normal acid. Their sum represents the total acidity produced by the compound on decomposition with water, and may be compared with the total acidity actually found by titration. These comparative figures are given in the following table :

Cubic Centimetres of Normal Acid.

Acidity from the sum of Br and F.	Acidity by titration.
(1) 2.72	2.62
(2) 10.02	9.96

General Conclusions.—Attempts to set forth regularities in the maximum valencies of elements depending on their position in the periodic table have always led to a distinction between two kinds of valency: that shown towards elements more electro-positive and that towards elements more electro-negative than the element in question. The former kind of valency has only one value in the case of the halogens; chlorine is only univalent towards hydrogen and also towards iodine (ICl_3 has been proved to possess the simplest formula). When we come to consider the compounds of halogens with more electro-negative elements, we are necessarily confined to their compounds with one another, since oxygen compounds cannot be considered as furnishing unimpeachable evidence in questions of valency.

The preparation of iodine pentafluoride for the first time fixed the maximum valency of iodine as not less than five. The existence of iodine trichloride shows that iodine cannot be more than trivalent

towards chlorine, and by analogy it cannot be more than univalent towards bromine, a fact established long since by Bornemann.

Similarly, the preparation of bromine trifluoride has fixed the valency of bromine as certainly not less than three. In this case also, the compound with chlorine exhibits a valency two less than that with fluorine. Bromine and chlorine will only combine to form the compound BrCl .

F	F	Cl	Br	I
Cl	F_3	(ClF)	BrF_3	IF_5
Br		Cl_2	BrCl	ICl_3, ICl
I			Br_2	IBr
				I_2

The symmetry shown by these compounds as tabulated is only partial, since a complete symmetry requires also the existence of ClF , BrF , IF_3 , and IF . It is by no means improbable that the last two are present in the dark liquid produced in the early stages when fluorine is allowed to react with iodine. Experiments, however, especially designed by other investigators to prepare ClF have always failed, whilst considerations mentioned above tend to show that BrF_3 is the only compound formed by fluorine and bromine.

PART II. *Fluorides of Selenium and Tellurium.*

Information as to fluorides of these elements is scanty and only qualitative. The fluorides described below are, as will be seen from the evidence, undoubtedly the characteristic and important and possibly the only fluorides of selenium and tellurium.

Moissan (*Le Fluor et Ses Composés*, p. 123) has described the appearance of the reactions between fluorine and these elements: "Selenium is attacked in the cold, there are abundant white fumes and the selenium presently melts and takes fire. Around it there is condensed a white, crystalline compound which is decomposed by water and dissolved by hydrofluoric acid. Powdered tellurium put in contact with fluorine combines with incandescence, giving abundant white fumes. The whole mass is quickly covered with a solid crystallised fluoride, easily volatile and very hygroscopic, having the aspect and properties of the fluoride of tellurium described by Berzelius."

Evidently these compounds needed much further study. The selenium used was Kahlbaum's best preparation, and the tellurium (kindly furnished by Dr. L. F. Guttman) had been purified by redistillation in a vacuum. The solids were contained in the horizontal part of a glass tube bent twice at right angles. One end fitted accurately over the copper tube delivering fluorine, the other

was furnished with a guard tube to prevent the entry of moist air. During the action of the fluorine, the appearances were on the whole as noted by Moissan. The incandescence of the tellurium takes the form of vivid blue sparks and the tube soon becomes heated. An important difference is that the white substance obtained was neither hygroscopic nor easily volatile.

The Solid Fluorides.—Although these solids did not appear to be very well-defined compounds, nevertheless some analyses were made of the white substance obtained by the action of fluorine on tellurium. The indefinite nature of this substance was borne out by the results, for whilst the first analyses gave 52.3 and 56.8 per cent. of tellurium, subsequent values were as far from this as 66.9 per cent. The method employed was to warm the substance contained in a glass tube with dilute caustic potash until all the white compound had dissolved, the tube was then washed out and the unchanged tellurium filtered off, dried, and weighed. The filtrate was then evaporated down with strong hydrochloric acid, diluted, and treated with sulphur dioxide until all the tellurium was precipitated. The weight of this gave the amount of combined tellurium, and the weight of white compound *plus* uncombined tellurium being known, the percentage of tellurium in the former could be calculated. This percentage varied widely, as stated above. Moreover, from other considerations it seemed likely that these fluorides would be not solids, but gases, or at least easily volatile liquids, for the fluoride of sulphur is described by Moissan as an extremely stable gas not easily liquefied (melting point, according to Moissan, -55°). It was to be expected that selenium and tellurium hexafluorides corresponding to sulphur hexafluoride would at any rate be stable enough to be isolated, and also that they would probably be gases or volatile liquids. For fluorine has a great tendency to form gaseous molecules with other elements. One need only compare silica with silicon fluoride. These considerations, together with the proved indefiniteness of the white compound, made me think that the real fluorides were still to be isolated.

Preparation of the Hexafluorides of Selenium and Tellurium.—A glass tube, of the form described above, containing the tellurium was joined to another which was kept at -78° . Immediately after the experiment, the second tube was isolated by sealing off while still in the freezing mixture. It was seen to contain a white, crystalline solid. When this was allowed to warm up, it changed first of all into a clear, mobile liquid, and then completely to the gaseous condition.

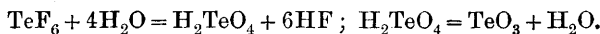
Density of Tellurium Fluoride.—As this gas was much compressed, it seemed worth while to attempt a rough measurement of the density. The sealed tube containing the gas was weighed, then attached to a Töpler pump, exhausted, and the gas collected over mercury. The

gas contained a little air. To determine the amount, it was allowed to stand over water (which completely decomposes tellurium fluoride), and the residual air afterwards measured. Neglecting the weight of that small volume of air and correcting all gaseous volumes to normal temperature and pressure, the density is obtained from the expression :

$$\frac{\text{weight of gas}}{(\text{total vol. of gas} - \text{vol. of air}) \times 0.0000896}$$

Two density determinations carried out by this method gave molecular weights of 257 and 240, which correspond very fairly to the theoretical 241.6 for tellurium hexafluoride. The density of the gas was afterwards determined accurately by Sir William Ramsay. The gas was first purified as follows (Fig. 1). The tap *T* was connected with a gas-holder in which the gas was stored, and *T*₁ with a Töpler pump. *T* being closed, the apparatus was completely exhausted through *T*₁. *T* and *T*₁ were then closed, and *T* opened gradually while the level of the mercury in the reservoir attached to the gas-holders was kept about half a barometer height below the level of that in the gas-holder. The gas slowly passed through *F*, which was immersed in liquid air. This process was repeated until all the gas had passed from the gas-holder through *F*. The air was finally pumped off until the mercury in *M* rose to the barometric height. The liquid air was then taken from the bulb *F*, and the hexafluoride pumped off and collected. This sample was then transferred to a gas burette and its density determined in the manner described by Ramsay and Travers (*Phil. Trans.*, 1901, Series A, 197, 53 and 54). The density (*O*=16) was found to be 119.5, the molecular weight therefore 239, corresponding to the formula TeF_6 .

Properties and Analysis of the Hexafluoride.—The gas has a very unpleasant odour, recalling that of tellurium hydride and also ozone. It is decomposed by water slowly but completely. If a sample is confined over water, scarcely any change is noticeable in half an hour, but in the course of a night the gas has been completely absorbed. On evaporating the solution in a platinum dish, a yellow residue of tellurium trioxide is left. By reducing this in a current of hydrogen and dissolving in concentrated sulphuric acid, the crimson colour characteristic of tellurium was produced. This reaction with water affords a method of analysing the gas. A known volume, implying a known weight of the gas, was allowed to stand over water for twenty-four hours, and the solution was then carefully evaporated to dryness and heated until its weight became constant at 150°. The percentage of tellurium was calculated from the weight of the trioxide.



Two analyses gave 50.06 and 51.9 per cent. of tellurium, the theoretical percentage of tellurium in TeF_6 being 52.6.

Selenium Fluoride.

Selenium fluoride was prepared in a similar way. In this case, the white solid in the reaction tube was not further examined. In the second tube, there appeared a white, crystalline mass. It was sealed off and then allowed to attain room temperature. The gas disengaged was collected over mercury. The density ($O=16$), determined in the same manner as that of TeF_6 , was found to be 97.23, giving a molecular weight of 194.46, the molecular weight for the simple molecule SeF_6 being 193.

This gas is more stable than tellurium fluoride; it decomposes water with extreme slowness, if at all. To a sample contained over mercury, a little water was added, and the position of the meniscus marked. After more than fifteen hours, there was no noticeable change in the position of the meniscus. The volumes of gas before and after treatment with water (corrected for the presence of water vapour and reduced to normal temperature and pressure) were 7.74 and 7.35 respectively. The gas does not combine with sulphur dioxide in the cold. A volume of selenium hexafluoride mixed with about five times its volume of sulphur dioxide shows no change in volume after mixing. On prolonged sparking, there is a slight contraction and a very small quantity of red solid, probably selenium, is deposited on the walls of the tube.

Physical Constants of the Hexafluorides of Sulphur, Selenium, and Tellurium.

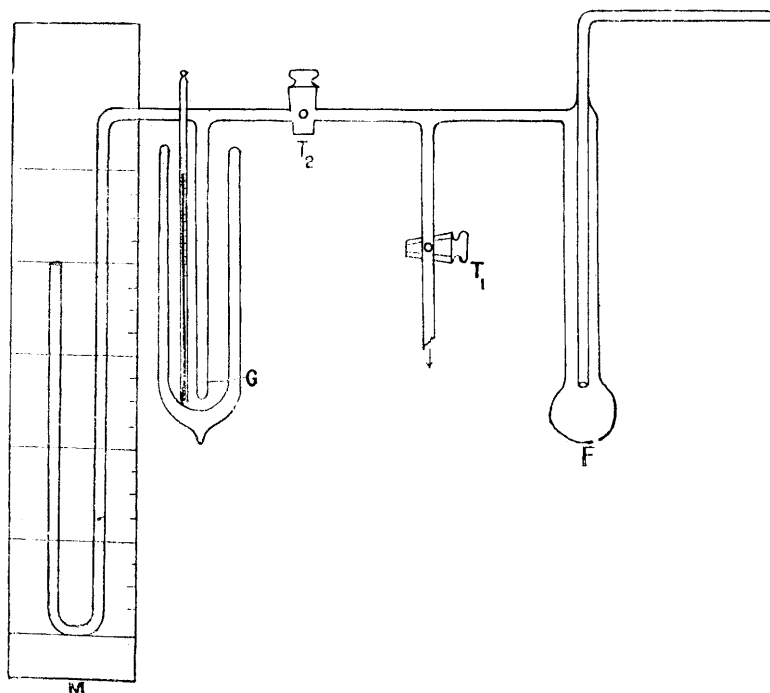
This series of compounds of exactly the same type presents well-marked regularities, some of which have not been observed before, and will probably have some value in connecting the physical properties of compounds with those of the elements which they contain. This series is quite unique in possessing the following properties.

- (1) All the compounds are stable gases and fairly easily manipulated.
- (2) They are all of the same type and exhibit the maximum valency of the elements which they contain, so that there are no disturbing influences due to "residual affinity."

These gases do not attack glass nor decompose spontaneously. They may be said, therefore, to be on the whole easily manipulated, but with one reservation. Both selenium and tellurium hexafluorides (but not the sulphur analogue) possess the annoying property of making mercury stick to glass in much the same way that ozone does,

with this difference, that there is no noticeable diminution in the volume of the fluorides. The mirror of mercury formed on the glass may render it difficult or even impossible to read the volume at some parts of the graduated burette. Also, when a thread of mercury is expelled from a capillary tube, the mirrors and even pools of mercury left sticking to the sides greatly interfere with such measurements as are carried out by bringing a uniform thread of mercury to some constant volume mark.

FIG. 1.



Measurements of Vapour Pressure.—The vapour pressures at various temperatures were measured in the apparatus indicated in Fig. 1.

The manometer of 3 mm. bore was fastened against a glass scale divided in millimetres. This form of manometer was rendered necessary by the fact that the volumes of gas condensed were small. Consequently the volume into which they expanded had also to be small in order that the vapour should remain saturated through a sufficient range of temperature. The whole apparatus was exhausted through T₁ by means of a Töpler pump. Then T₁ and T₂ were closed, the fractionating bulb F was immersed in liquid air, and the gas

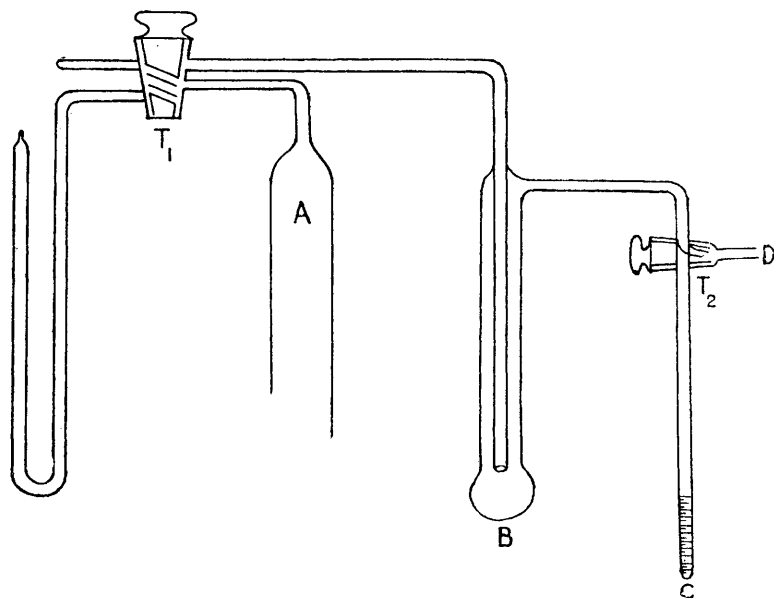
gradually admitted from a gas-holder. The fluorides condensed in *F*, and any air was removed by opening *T*₁ and again exhausting; *T*₁ was then closed, *T*₂ opened, and the vessel of liquid air was transferred from *F* to the side-tube *G*. The gas quickly condensed into *G* and the tap *T*₁ was again opened for a moment. The manometer then showing a vacuum, *T*₂ was closed and the side-tube allowed to remain for five minutes in the liquid air. The pressure did not alter, showing that the vapour pressures of these compounds are nothing at the temperature of liquid air contained in an open vessel. The liquid air was then replaced by ether or ligroin (preferably the former) cooled with liquid air to about -110° . The temperature rose quite slowly and was registered by means of a pentane thermometer immersed in the bath. The manometer was constantly tapped before the reading, which was taken as nearly as possible at the same time as that of the temperature. In the case of selenium and tellurium hexafluorides, the tube soon became coated with mercury as described above, so that readings of the closed limb had to be abandoned. The heights of mercury in the closed limb corresponding to heights in the open limb were in these cases read off from a line which had been plotted by finding many corresponding values of readings on the two limbs. The smoothed curves are given in Fig. 3. The curve very quickly becomes steep in the case of sulphur hexafluoride, but alters its slope more slowly in the case of selenium and tellurium hexafluorides, the vapour pressure curves of which resemble one another very closely and are separated by only a narrow temperature interval (3.5° at the boiling point). The interval between the curves for the sulphur and selenium compounds is on an average 23° . The points where the pressures of the solids become 760 mm. are respectively 211° , 234° , 237.5° . This temperature was found by a short extrapolation in the case of the sulphur compound, of which there was not a sufficient quantity to give a saturated vapour above 209° .

Melting Points.—The gases were next sealed up in capillary tubes as follows (Fig. 2). The gas was measured and transferred to the gas-holder *A*. The whole apparatus up to *T*₁ (closed) was then exhausted through *D*. *B* was then placed in liquid air, *T*₁ opened to *B*, and the gas allowed to pass slowly through *B* until the mercury was beyond *T*₁. *T*₂ was then opened and the solid fluoride completely freed from any trace of air by exhausting through *D*. *T*₂ was then opened to *C*, which was a capillary tube graduated in millimetres and calibrated by running in and weighing a thread of mercury. The liquid air was now transferred from *B* to *C* and the vessel was gradually raised. The gases condensed as a white snow, further up the tube the solids appeared as crystalline spangles. The capillary tube was placed for a moment in connection with the vacuum and then sealed off. These

tubes then contain known volumes of the gases existing as liquids under high pressures. The melting points were determined by immersing the tubes in ether cooled by liquid air to some temperature below the solidifying points. The temperature of such a freezing mixture contained in a vacuum cylinder rises quite gradually, and the intervals between the first appearance of liquid and the slipping down of the solid were on an average 1° . The latter temperature was chosen in each case. The melting points are given in a table, and are also indicated by crosses on the P , T , curves (Fig. 3).*

It will be noticed that the line joining the melting points of sulphur

FIG. 2.



and selenium hexafluorides slants slightly upwards and, if continued, cuts the curve for the tellurium compound at about 241° . The melting point of the last substance is abnormally low, this being almost the only irregularity exhibited by this series of compounds.

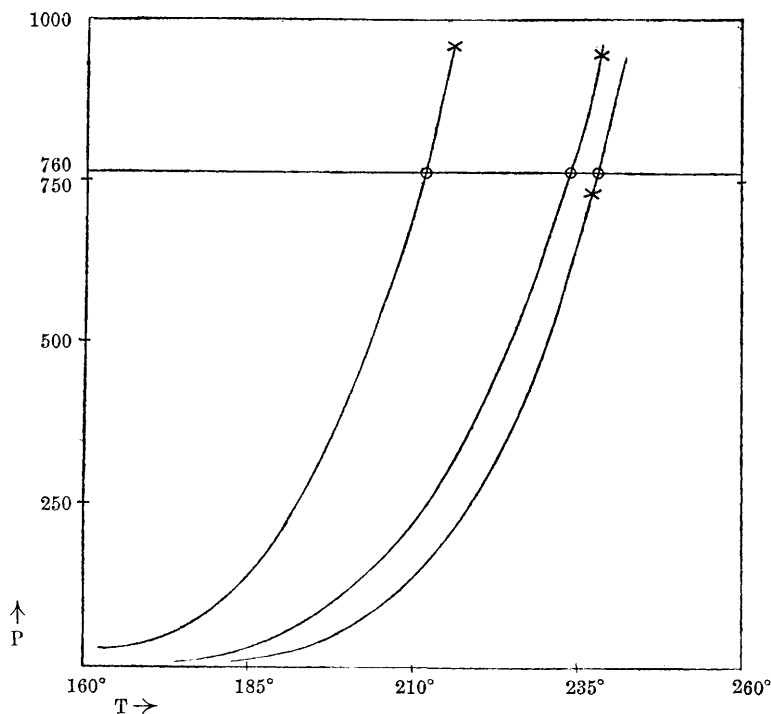
Critical Temperatures.—The tubes were gradually heated in a beaker of water. Since they were from one-third to one-half full of liquid at the ordinary temperature and the critical volume is usually taken as three times the volume of the liquid, the capacity of the tube was approximately equal to the critical volume of the gas. Temperatures

* Moissan and Lebeau have found the melting point of sulphur hexafluoride to be -55° .

were read when the extremely fine line of flattened meniscus vanished and when it reappeared from a band of mist. These temperatures were not more than 1° apart and their mean was taken as the critical temperature. The points are: for SF_6 , 327° abs. (54°); SeF_6 , $345\cdot35^\circ$ abs. ($72\cdot35^\circ$); TeF_6 , $356\cdot25^\circ$ abs. ($83\cdot25^\circ$).

	Difference of boiling points.	Difference of critical temperatures.
$\text{SeF}_6 - \text{SF}_6$	23°	$18\cdot35^\circ$
$\text{TeF}_6 - \text{SeF}_6$	$3\cdot5$	$10\cdot9$
$\text{TeF}_6 - \text{SF}_6$	$26\cdot5$	$29\cdot25$

FIG. 3.



If, then, the critical pressures are approximately equal (that is, within 50 mm., which is the alteration of pressure caused by rise of 1°), the P , T , lines of tellurium and selenium hexafluorides have much the same separation at the critical temperatures as at the temperatures recorded on the curves, but the selenium hexafluoride line bends considerably from that of the tellurium towards that of the sulphur analogue.

In the following table are given the melting points, T , boiling points,

T_1 , and critical points, T_2 , of these gases, and also T' and T_1 for the series SH_2 , SeH_2 , and TeH_2 as determined by Forcrand and Fonze-Diacon (*Compt. rend.*, 1902, 134, 1209). It will be noticed that the differences between T' and T_1 are approximately equal in the case of sulphur and selenium hydrides as well as the corresponding fluorides, but that whilst $T - T_1$ is much greater in the case of tellurium hydride, it is much less in the case of tellurium hexafluoride, the melting point of which is very nearly equal to its boiling point. Also the melting points of the hydrides are below their boiling points, whilst the melting points of the fluorides are above the temperatures at which the vapour above the solid attains a pressure of 760 mm.

Compound.	T .	T_1 .	T_2 .	$T - T_1$.
SF_6	-56°	-62°	$+54^\circ$	6°
SeF_6	$-34\cdot5$	-39	$+72$	$4\cdot5$
TeF_6	-36	$-35\cdot5$	$+83$	$-0\cdot5$
SH_2	-86	-62	—	-24
SeH_2	-64	-42	—	-22
TeH_2	-48	0	—	-48

Coefficients of Expansion.—The above-mentioned calibrated tubes were placed in baths at the required temperature and the volumes of the liquids calculated from the positions of the meniscus on the scale. The expansion is therefore that of the liquid under pressures equal to its own vapour pressures at the temperatures under consideration. It has been abundantly shown that the expansion of a liquid is scarcely affected by pressures of this order. The temperature intervals were chosen such that the lower temperatures were about equal distances above the respective melting points, and the highest temperatures were so far below the critical points as to avoid the abnormal expansion which liquids display near those points.

	Temperature interval.	Coefficient of expansion.
SF_6	$-18\cdot5^\circ$ to $+30^\circ$	0·027
SeF_6	$-3\cdot5$ „ $+51$	0·030
TeF_6	$-3\cdot5$ „ $+51\cdot5$	0·032

Specific Gravities of the Liquids.—The volumes of the gases sealed in the tubes being known, as well as the volumes of the liquids formed by their condensation, the specific gravities could be determined. Two series of experiments were made; one in which the capillary tubes were closed by a tap during the observation, and another in the above-mentioned sealed tubes. The absolute values found in each set of observations differ somewhat, but, taking each set separately, the same relation holds between the molecular volumes of the three liquid compounds. I have chosen the second set because they were more carefully carried out and the method is more accurate. The volumes in the immediate neighbourhood of the melting points

being rather irregular, the specific gravities were necessarily taken at some distance above these, the temperature differences being 12° , 11° , and 11.5° respectively.

Boiling point.	Temperature for specific gravity.	Specific gravity.	Molecular volume.
-62°	-50°	1.91	76.5
-39	-28	2.51	77.2
-35.5	-24	3.025	79.9

The close agreement of these molecular volumes accords well with a hypothesis that molecular volumes of binary compounds are conditioned solely by the type of the compound and the nature of the element of smaller valency. On examining other series to see if the like held in their case, it was evident that care had seldom been taken to choose corresponding temperatures for the determination of specific gravity. In the following table, the numbers in brackets indicate the number of degrees between the temperature of the observation and the boiling point of the liquid concerned. In cases where the temperature has not been given, the specific gravity was probably determined at about 15° .

OH_2 .	SH_2 .	SeH_2 .	TeH_2 .
18.8 (0°)	39.53 (—)	38.2 (—)	49.75 (-20°)
	PCl_3 .	AsCl_3 .	SbCl_3 .
	93.5 (0°)	84 (-110°)	85 (-150°)
CHCl_3 .	SiHCl_3 .		
85.5 (0°)	94 (—)		

It is to be regretted that the data are so scanty. The numbers at least point to a probability that this regularity will be found to hold in other series, since there is no wide difference between the numbers except in the case of water. The densities of arsenious and antimonious chlorides determined at 110° and 150° respectively below their boiling points are hardly comparable with that of phosphorus trichloride determined at its boiling point. Evidently the molecular volumes of the two former chlorides will approach that of the latter as the temperatures of the liquids approach their respective boiling points. The fluorides of sulphur, selenium, and tellurium form the only series of three which shows a very close agreement, but they are also the only series of three the molecular volumes of which have been measured at corresponding temperatures. Denoting by the word "similar" a series of compounds in which the atoms of higher valency belong to the same vertical groups in the periodic classification by long periods (double octaves), and the atoms of lower valency are the same throughout the series, it may be provisionally stated that "equal"

volumes of "similar" liquid compounds at corresponding temperatures contain the same numbers of molecules, or, in other words, compounds belonging to "similar" series are always associated to the same extent in the liquid state when the vapour pressures of the liquids are equal.

Refractivities of the Gases.

The refractivities were kindly determined for me by Mr. Cuthbertson and Mr. Metcalfe, using the method of interference due to Jamin. Interference bands were counted for differences of pressure amounting to 70 and 80 mm. The refractivities were calculated by

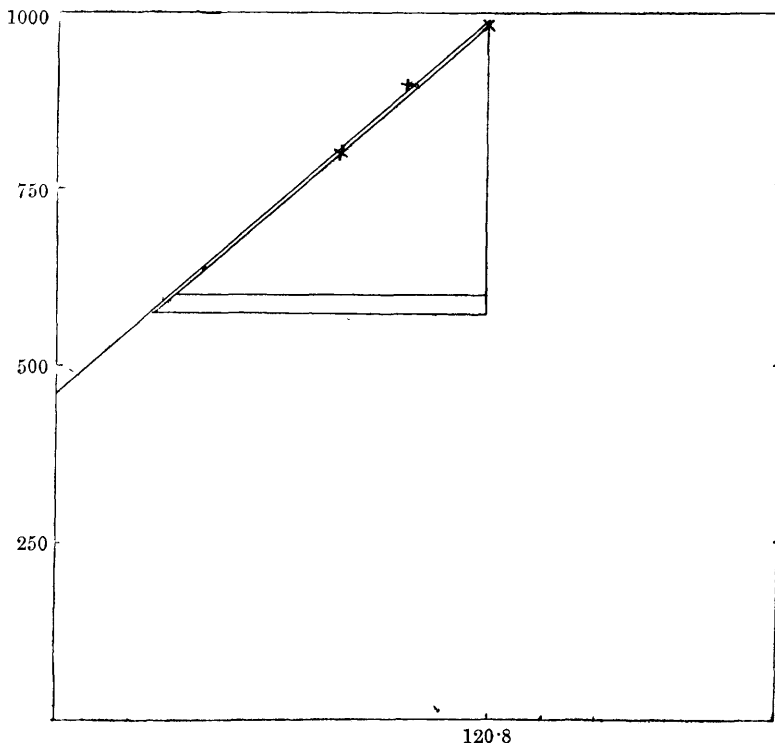
the formula $\mu - 1 = \frac{5893 \times \text{No. of bands} \times T \times 760}{\text{Length of tube} \times 273 \times P}$. The values found

were most remarkable when compared with those obtained from compounds formerly examined. These have usually shown a rough approximation to an additive law, although in some cases they vary more than 20 per cent. from the value required by such a law—a variation too great to be accounted for by experimental error. In the case of sulphur, selenium, and tellurium hexafluorides, there is no approach to an additive law, the refractivities found being 783, 895, and 991, while those calculated from $3F_2 = 576$, $S = 540$, $Se = 810$ ($3/2 \times 540$), $Te = 1350$ ($5/2 \times 540$) (according to Cuthbertson's law connecting the refractivities of the elements) are 1116, 1386, and 1926 respectively. The refractivity of tellurium hexafluoride is actually less than that calculated for one atom of gaseous tellurium. There is, however, a regularity connecting these refractivities with the densities of the gases, which is shown in Fig. 4. The refractivities plotted against the densities fall very close to a straight line. The theoretical densities calculated from the atomic weights were chosen, since these depending on the results of analysis are probably more accurate than the densities obtained by weighing the gases.

If the points for sulphur and tellurium hexafluorides are joined by a straight line, this cuts the ordinate from 96.5 at 884, eleven units away from the observed refractivity 895. Thus, if the refractivity of the selenium analogue were unknown, it could be calculated within 2 per cent. from those of the sulphur and tellurium compounds. The experimental error in determining these refractivities being about 2 per cent., it is quite certain that the refractivity *minus* any number greater than 500 (where the line cuts the ordinate from the origin of densities) is proportional to the density. The reason that this relationship has never been observed before, is that no such series has ever been examined before in this way. The only series of three compound gases the refractivities of which have been determined, is that of the halogen hydrides. In their case, $\mu - 1$ for hydrogen bromide found

by joining the points for the chloride and iodide lies about 10 per cent. below $\mu - 1$ actually observed. The indices of refraction for the series, hydrogen chloride, &c., are difficult to determine accurately on account of the hygroscopic and corrosive nature of the gases. It seems extremely probable that when the refractivities of other comparable series have been accurately determined the same relation will

FIG. 4.



Ordinates = $\mu - 1$ for SF_6 , SeF_6 , TeF_6 .

Abscissae = Densities of SF_6 , SeF_6 , TeF_6 .

$\text{SF}_6 = 73, 783$; $\text{SeF}_6 = 96.5, 895$; $\text{TeF}_6 = 120.8, 991$.

Refractivities and densities of the fluorides of sulphur, selenium, and tellurium.

be found to hold, although no doubt the characteristic slope of the line would be different in each case.

The points have been marked where the line cuts the ordinate from F_6 ($d=57$) and F_2 ($d=19$). The latter point gives an index of 552, which is within 5 per cent. of the index for 3F_2 (576). At present this can only be regarded as a coincidence.

If the assumption is made that $\mu - 1$ for F_6 in such a combination remains constant throughout the series, this value subtracted from the refractivities will give the retardation due to sulphur, selenium, and tellurium in combination. These values, 207, 319, and 415, are very nearly in the ratio 4, 6, and 8. The ratios of $\mu - 1$ for the elements according to Cuthbertson's law (*Phil. Trans.*, 1905, Series A, 204, 323) of simple integers should be 4, 6, and 10. There is no explanation at present of the variation in the case of tellurium, but the simplicity of the relation is noteworthy.

This law connecting the refractivities of compounds with the alteration of density caused by the substitution of an element of higher atomic weight may be compared with the well-known law connecting refractivities with alterations of density caused by compression of the same gas. This relation, $\frac{\mu - 1}{d} = \text{a constant}$, is universally employed in order to render comparable the results of refractivities determined at different pressures.

The above-mentioned regularity shows that if $(\mu - 1)_c = \text{refractivity of the compound}$, $K = \text{any number greater than 450}$: $\frac{(\mu - 1)_c - K}{d} = \text{a constant}$.

In conclusion, I desire to express my thanks to the Royal Society for a grant in aid of this research, to Sir William Ramsay for his valuable advice and assistance, and to members of the Staff at University College for the kind interest they have shown in this investigation.

HERIOT-WATT COLLEGE,
EDINBURGH.
