295. *The Preparation and Properties of Disulphur Decafluoride.*

By Kenneth G. Denbigh and Robert Whytlaw-Gray.

The Fluorides of Sulphur.—Sulphur hexafluoride was first prepared by Moissan and Lebeau (*Ann. Chim. Phys.*, 1902, **26**, 145) and found to be highly stable, being unattacked by potassium hydroxide solution and decomposed by sodium only at the boiling point. Prideaux (J., 1906, **89**, 316), Klemm and Henckel (*Z. anorg. Chem.*, 1932, **207**, 73), and Schumb and Gamble (*J. Amer. Chem. Soc.*, 1930, **52**, 4302) have measured most of its physical properties. Pauling and Brockway (*Proc. Nat. Acad. Sci.*, 1933, **19**, 68), from electron-diffraction experiments, found that the fluorine atoms lie at the corners of a regular octahedron, and their results also suggest that the gas has an ionic structure. Watson, Rao, and Ramaswamy (*Proc. Roy. Soc.*, 1934, **143**, *A*, 558) measured its dielectric constant, and found that it has no moment; also, on samples supplied by us, the coefficient of gaseous expansion (Coppock and Whytlaw-Gray, *Proc. Roy. Soc.*, 1934, **143**, *A*, 487) and the parachor (Pearson and Robinson, J., 1933, 1427) have been measured.

Ruff (*Z. anorg. Chem.*, 1911, **72**, 63, 329) found evidence for formation of another fluoride of sulphur when metallic fluorides were heated with sulphur; and Centnerszwer and Strenck (*Ber.*, 1923, **56**, 2249; 1925, **58**, 914) examined the gas obtained by heating silver fluoride with sulphur and stated that it has the formula S_2F_2 and is absorbed by potash solution. Fischer and Jaenckner (*Z. angew. Chem.*, 1929, **42**, 810) have similarly heated cobalt fluoride with sulphur, and state that the gas formed has the formula SF_4 and is also absorbed by potash solution.

Two oxyfluorides of sulphur, SOF_2 and SO_2F_2, have also been described by Moissan and Lebeau (*loc. cit.*).

We recently had occasion to prepare a large quantity of sulphur hexafluoride by passing fluorine over sulphur, and we examined the products, the chief result being the isolation of *disulphur decafluoride.*

EXPERIMENTAL.

The fluorine was prepared by electrolysing potassium hydrogen fluoride in a copper cell of modified design, using a graphite anode (Denbigh and Whytlaw-Gray, *J. Soc. Chem. Ind.*, 1934, **53**, 138T); it was purified from hydrogen fluoride by passage first through a long tube packed with sodium fluoride, and then over highly pure sulphur contained in a copper tube. All air had been expelled from the apparatus with a current of nitrogen before the preparation was started.

The sulphur fluorides were condensed in a liquid-air trap. Four products were obtained in the following order of decreasing volatility :

(A) Sulphur hexafluoride, which *sublimed* out of the liquid-air trap and was not absorbed by concentrated potassium hydroxide solution.

(B) A gas which volatilised from the *liquid* state and was rapidly absorbed by potash solution (this gas had been observed but not investigated by Moissan and Lebeau); this was purified, and its vapour density determined (*M*, 102·6). It may be S_2F_2 (*M*, 102) (cf. Centnerszwer and Strenck, *loc. cit.*); its properties are similar to those described for the difluoride, except that our gas has a lower vapour pressure (b. p. *ca.* −50°). We believe that Centnerszwer's product contained some very volatile impurity.

(C) A very volatile liquid which remained in the trap after (A) and (B) had both volatilised off; it could be readily vaporised by warming with the hand and, like the hexafluoride, was not absorbed by potash solution.

(D) A residual oil which could not be vaporised by warming with the hand.

Attention was directed to the gases not absorbed by alkali, *i.e.*, the hexafluoride and (C). The mixture was stored in a gasometer over a strong caustic potash solution, dried, and fractionated into three parts, the vapour densities of which were measured on a microbalance.

Fraction 1. The most volatile fraction had a molecular weight considerably below the value for the hexafluoride. A systematic examination showed this to be due to the presence of carbon tetrafluoride, a pure sample of which was isolated; this gas was evidently formed by attack of the graphite anode of the fluorine cell : its properties have been investigated by Ruff and Keim (*Z. anorg. Chem.*, 1930, **192**, 249).

Fraction 2. The molecular weight of the middle fraction was slightly below the value for the hexafluoride. This may have been due to the higher homologues of carbon tetrafluoride (cf. Ruff and Keim, *loc. cit.*).

Fraction 3. The least volatile fraction had a molecular weight considerably above that of the hexafluoride; this might have been due to some new fluoride of sulphur or to carbon fluorides, or to both. A sample of this fraction was decomposed by heating with sodium, and free carbon was obtained; its quantity, however, did not appear commensurate with the quantity of the sample decomposed, and it appeared probable, therefore, that the volatile liquid, (C), whose vapour was contained in Fraction 3, did not consist entirely of carbon fluorides, but might contain some new sulphur fluoride.

In order to prepare a pure specimen of sulphur hexafluoride, and to investigate whether (C) or (D) contained any new sulphur fluorides, it became necessary to get rid of the carbon fluorides. Since there is a long series of these compounds, they could not be eliminated by fractionation, so their absence had to be ensured before the sulphur fluorides were formed. After unsuccessful attempts with anodes other than graphite, recourse was had to passage of the fluorine through a copper U-tube immersed in liquid oxygen (b. p. of fluorine, − 187°; oxygen, − 183°). By this procedure all the carbon fluorides were trapped with the exception of the tetrafluoride (b. p. − 130°), which was easily eliminated by subsequent fractionation (b. p. of SF_6, − 62°).

A large quantity of sulphur fluorides was prepared by this method, and the product (D) was now absent, but (A), (B), and (C) were still obtained. As before, the gas was kept over potassium hydroxide solution for some time, the product (B) and any silicon fluorides being thereby removed. The two components of the unabsorbed gas, *viz.*, the hexafluoride and (C), were separated by repeated fractionation.

A sample of the hexafluoride was obtained in a highly pure state by drying, repeated fractionation, and by repeated passage over liquid sodium–potassium alloy. This gas had a molecular weight of 146·0 ± 0·1 (calc., 146·06). We believe it to be the purest sample yet obtained, since no previous workers have eliminated carbon fluorides and many have not even displaced air from their apparatus, so that the possibility of the formation of oxyfluorides was not excluded.

The other constituent, the vapour of the volatile liquid (C), was repeatedly fractionated, and finally obtained with *M* 260·2, unchanged by further fractionation. It appeared probable that this substance was *disulphur decafluoride* (*M* 254) (see Nature, 1933, **131**, 763), and we therefore attempted to prepare it in larger quantities.

Preparation of Disulphur Decafluoride.—Unsuccessful methods were (i) passage of the hexafluoride over heated catalysts; (ii) modification in the proportion of sulphur and in the temperature in the original method. Somewhat better yields, however, were obtained by filling the reaction tube with plastic sulphur instead of with ordinary, rhombic sulphur; even this method gives only very small quantities of the substance: from about 20 l. of hexafluoride, about 0·1 c.c. of highly pure liquid (*i.e.*, 20 c.c. of vapour) was obtained. This was used for measurement of all the physical properties, and about the same quantity of a slightly less pure sample was used for a study of the chemical properties. A further quantity of a highly pure sample was obtained for the analysis. The method of eliminating carbon fluorides, already described, was used in preparing these samples.

Fractionation.—A special method of fractionation was evolved in order to minimise loss; this was carried out in two stages. The first stage consisted of a fractionation under 2 atm., the vapour-pressure curves of solid hexafluoride and of liquid decafluoride being found to be farther apart at this than at lower pressures. The apparatus (Fig. 1) consists of a vessel (*a*) and a manometer (*b*) connected to the gas train through the pressure tap (*c*). The lower part of (*a*) consists of a small bulb (*d*) connected to the main part through a narrow neck (*e*). The mixture of hexafluoride gas and decafluoride vapour was condensed in the upper part of (*a*), and the temperature allowed to rise slowly. The liquid ran down into the bulb and left the solid hexafluoride in the upper part of the vessel, where it sublimed slowly. When the pressure reached 2 atm., the tap was opened slightly to allow the gas to pass off, and fractionation was continued at this pressure till only the liquid remained.

The latter was still by no means pure, since it contained much dissolved hexafluoride. It was, therefore, transferred to a small fractionating column (Fig. 2), of internal volume *ca.* 3 c.c. The liquid was condensed in the lowest bulb (b_1), and the vessel surrounding the four higher bulbs was filled with acetone and solid carbon dioxide. The liquid decafluoride was allowed to attain room temperature, so that it boiled rapidly and, condensing in the column, ran back into (b_1) through the jet (j_1). The hexafluoride did not condense, however, but passed off through the tap (*t*).

The two stages of the above fractionation were both very efficient. The product obtained was sometimes not quite pure but needed one or two simple fractionations before it attained perfectly constant vapour pressure.

Vapour Density.—The sample thus obtained was divided into three portions by a further fractionation, and the vapour densities of these were measured on the microbalance (which balanced in pure dry air at 621·91 mm. at 18·5°). The balancing pressures of the three fractions at 17·8° were: most volatile fraction, 68·93 mm.; middle fraction, 69·00 mm.; least volatile fraction, 68·60 mm. This agreement (to within 0·6%) means that the gas was homogeneous, and the liquid was therefore not a mixture (since the three fractionations had been carried out at different pressures, a constant-boiling mixture was also excluded).

The molecular weight computed from the mean balancing pressure, 68·8 mm., is 259·5 (cf.

260·2, above, on a different sample). The excess above the calculated value (254) is due to the high adsorption on the microbalance, which was of the uncompensated type.

Analysis.—The analysis was a matter of considerable difficulty, but four determinations were carried out.

(1) A quantity of the vapour was decomposed by several hours' sparking with hydrogen in a glass vessel coated internally with a thin layer of potassium hydroxide. Hydrogen fluoride and sulphide were formed and were absorbed by the potash, which became yellow, but the glass was not attacked. The apparatus was dismantled, washed out with water, and fluorine determined as lead chlorofluoride in one half of the solution, and sulphur as barium sulphate (after oxidation with sulphur-free ammoniacal hydrogen peroxide) in the other half (Found : S : F = 1 : 4·91).

FIG. 1.

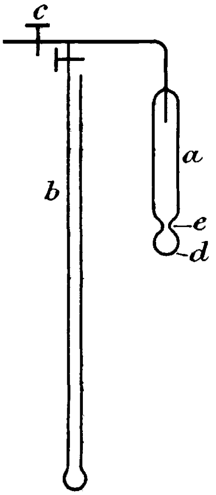


FIG. 2.

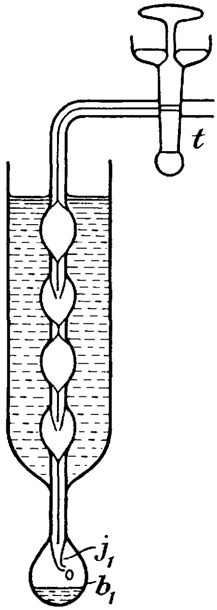
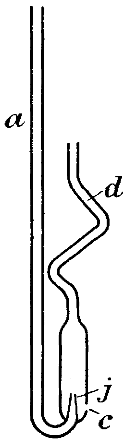


FIG. 3.



(2) Decomposition was carried out as before, but the sulphur and fluorine were determined by a different method. The solution was first oxidised with ammonia and perhydrol, silica removed by the method of Hoffman and Lundell (*Bur. Stand. J. Res.*, 1929, **3**, 581), and calcium fluoride precipitated and weighed, a little sodium chloride having been added previously to increase the solubility of calcium sulphate; finally, barium sulphate was precipitated and weighed (Found : S : F = 1 : 5·01). The whole method was first checked on a standard solution of sodium fluoride and sulphide and found to be satisfactory.

(3) and (4) Decomposition was carried out in a different way : a small boat containing pieces of dry sodium was heated in the vapour of the liquid by means of a platinum coil, the leads being sealed through the glass containing vessel. The decomposition took place with great vigour at the m. p. of sodium, the whole of the gas burning with a brilliant incandescence in contact with the sodium vapour; reaction appeared to be complete within a few seconds. The mixture of sodium fluoride and sulphide was dissolved in water, and the solution divided into two parts, in both of which the sulphur and fluorine were estimated by the method in (2) [Found : S : F = (i) 1 : 4·81; (ii) 1 : 4·85].

These results, in conjunction with the fractionation to constant vapour pressure and density, and the proof that the substance was not a constant-boiling mixture, establish beyond doubt that the compound was disulphur decafluoride.

Whilst preparing the hexafluorides of selenium and tellurium, Yost and Claussen (*J. Amer. Chem. Soc.*, 1933, **55**, 885) obtained substances, which, from vapour-density measurements, they believed to be the octafluorides; they may, however, have been impure samples of the decafluorides, analogous to our compound. Also, Watson, Rao, and Ramaswamy and Centnerszwer and Strenck (*locc. cit.*) obtained traces of a volatile liquid which was probably our decafluoride.

Chemical Properties.—At room temperatures, the compound is a colourless, very volatile liquid whose vapour has a smell resembling that of sulphur chloride or sulphur dioxide. It solidifies in liquid air to an opalescent solid which melts to a very mobile liquid. Owing to the small quantity available, only a few experiments were possible.

The vapour is insoluble in and unattacked by water, and also practically unattacked by concentrated potassium hydroxide solution. It is, however, decomposed by the molten alkali, yielding potassium compounds of sulphur and fluorine.

Ordinary tap greases were blackened by the vapour, with simultaneous deposition of sulphur on the glass. Mr. Bradley, of this Department, kindly lent us a grease composed of paraffin and paraffin wax, which was unattacked and has been used extensively in the research.

To investigate the action of metals, small coils were electrically heated in about 1 c.c. of vapour contained in a silica bulb. Platinum was not attacked in the cold, but at a bright red heat it reacted, a pale yellow substance being deposited on the walls. Iron was blackened at a fairly low temperature, and at a bright red heat there was vigorous attack, with deposition of white clouds on the walls of the bulb. Copper was not attacked in the cold, but behaved similarly at a bright red heat, the deposit being pale yellow and the metal blackened. Mercury was also unattacked in the cold if pure, but at its b. p. there was ready reaction with formation of a black and a yellow substance.

In these reactions with metals, the white or yellow deposits appear to be the slightly volatile metal fluorides mixed with free sulphur, and the black deposits were found to be metal sulphides. In every case, except with sodium (see p. 1349), a new gas was formed which was slightly soluble in potash solution. This may have been one of the lower fluorides of sulphur, but there was too little for identification.

Silica was attacked by the gas at a red heat, and at a lower temperature in presence of sulphur, with production of silicon tetrafluoride and sulphur dioxide in each case; the latter reaction appears to be analogous to one which Moissan noted for the hexafluoride : $2SF_6 + S + 3SiO_2 = 3SiF_4 + 3SO_2$; $2S_2F_{10} + S + 5SiO_2 = 5SiF_4 + 5SO_2$. A rough estimation showed that our reaction appeared to follow this equation.

In general, the gas is much less inert than the hexafluoride.

Vapour Pressure.—For a measurement of the vapour pressure, a simple mercury manometer connected to a bulb immersed in a cold bath was used. The bath consisted of acetone, contained in a high-quality vacuum vessel, the acetone having been cooled previously by pouring liquid air into the vessel. The bath was kept stirred by blowing in the cold air given off by a large quantity of evaporating liquid air. A special bubbler was used (Fig. 3), the cold air being blown in through the tube (*a*) and emerging through the jet (*j*). The acetone enters through the hole (*c*) and is lifted by the air stream to the top of the tube (*d*). The bath was extremely satisfactory, the rate of rise of temperature being only 0·5° in 20 minutes at − 50°.

The temperature of the bath was measured by a vapour-pressure thermometer, liquid sulphur dioxide being contained in a bulb identical with, and touching, the bulb containing the liquid decafluoride. The measurements of Stock, Henning, and Kuss (*Ber.*, 1921, **54**, 1119) were used in computing the temperature. For temperatures above − 10° a highly accurate mercury thermometer was used.

Two series of observations, A and B, were made, the gas being refractionated between them. The results are shown in the following table, the vapour pressure (p) of the decafluoride being

Temp.	*p*.	Temp.	*p*.	Temp.	*p*.	Temp.	*p*.	Temp.	*p*.
				Series A.					
−56·1°	7·78	−36·2°	31·7	−25·4°	64·7	−14·0°	119·1	7·3°	322·5
−48·2	14·3	−35·8	31·5	−20·1	90·2	− 7·6	163·6	12·8	416·0
−41·6	22·2	−31·2	43·5	−18·6	93·4	0·3	235·0	14·4	434·3
				Series B.					
−41·3	22·6	−24·4	66·3	−17·1	98·8	0·0	229·9	20·9	561·0
−28·6	51·4	−21·8	76·7	−14·5	113·0	14·4	433·2	22·4	595·3

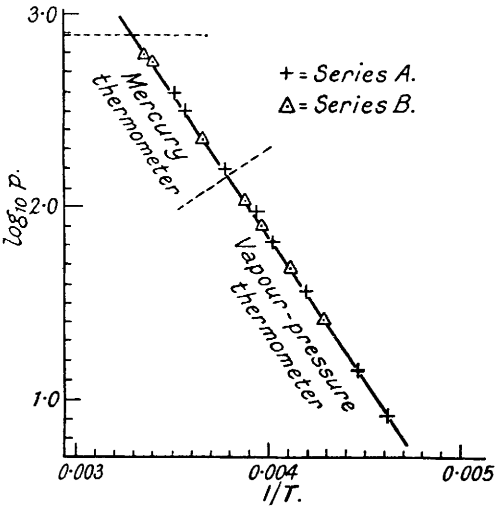
given in terms of mm. of mercury at 0°. The experimental error in each measurement is about 1%. The graph results have been plotted as $\log_{10} p$ against $1/T$ (Fig. 4); practically all the points fall on the line, which has a very slight curvature. Both series conform to the same line, and the results with the vapour-pressure thermometer agree closely with those from the mercury thermometer. The line can be represented by the equation $\log_{10}p = -1530/T + 7{\cdot}95$. A short extrapolation shows the b. p. to be 29° ± 1°. The molecular latent heat of vaporisation, calculated from the slope, is 7000 cals., and the Trouton constant (23·0) is normal; for the hexafluoride the respective values are 5640 cals. and 25·8.

Melting Point.—The m. p. has been measured by Stock's method (*Ber.*, 1917, **50**, 157), depending on the temperature at which a glass style slides through the melting solid. A calibrated pentane thermometer was used. The following five readings were taken: – 93·0°, – 91·3°, – 92·8°, – 90·8°, – 91·2°, and after refractionation two readings were – 91·7° and – 92·0°, the agreement showing that the substance, which had a constant vapour pressure and vapour density, had also a constant m. p. The mean of all seven values is – 92° ± 1°.

Liquid Density at 0°.—This constant was measured by condensing a known volume of the gas, from a carefully calibrated point burette, at a measured temperature and pressure, in a capillary tube (of 1 mm. bore, and accurately calibrated with mercury) immersed in melting ice. The volume of the liquid and the saturated vapour in the capillary were read, and after corrections for the deviation of the gas from Boyle's law, a value for the liquid density was obtained. The condensation was carried out rapidly so that the mercury rose quickly inside the burette, thus preventing vapour adsorbed on the walls from being condensed. The following six values (g./c.c.) were obtained at 0°: 2·05, 2·11, 2·07, 2·04, 2·07, 2·11; mean 2·08 ± 0·03.

FIG. 4.

Vapour pressure of S_2F_{10}.



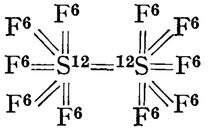
Surface Tension at 0°.—The measurement of this property presented difficulty, since less than 0·1 c.c. of liquid was available. A narrow, flat-bottomed, glass tube containing two vertical capillaries, slung from a blue glass hook, was finally used (Sugden, "The Parachor and Valency"). The capillaries were checked for circularity and a suitable difference in radii before being used. The tube containing the capillaries was immersed in an acetone–carbon dioxide bath, and the decafluoride vapour was admitted through a tap. The bath was then replaced by one of ice-water, contained in an unsilvered Dewar vessel. The meniscuses in the two capillaries therefore *fell slightly* owing to the rise in temperature. This method, therefore, secured *wetting* of the glass capillaries by the liquid at the temperature of measurement.

When temperature equilibrium had been attained, the difference in height of the meniscuses in the capillaries was measured with a microscope reading to 0·001 mm. The liquid was then allowed to evaporate, recondensed, and a fresh reading taken as before. After eight readings, the capillaries were taken out and cut at the points at which the meniscuses had been; their radii were measured in three directions:

Tube 1. Mean radius 0·0144 cm. ± 2%.
Tube 2. „ „ 0·0272 cm. ± ½%.

The differences in height, H, of the liquid in the two tubes at 0° were: 0·4460, 0·4444, 0·4485, 0·4593, 0·4472, 0·4462, 0·4521, 0·4563 cm.; mean 0·450 cm., whence γ = 13·9 dynes/cm. ± 3%.

Parachor.—The two foregoing constants give a value of 236 ± 4 for the parachor. This is in fair agreement with the following structure (*P*, calc., 243), which moreover, appears most probable on chemical grounds:



In calculating the parachor, we have assumed the normal valency of sulphur to be 2, and have used the decrement of 12·8 units which Sidgwick and Bayliss (J., 1930, 2027) found to take place in the parachor when the covalency of hydrogen is increased from 1 to 2; *i.e.*, 2S + 10F – 8 × 12·8 = 345 – 102 = 243 units. It is possible that for sulphur the decrement due to the covalency increase would be greater than for hydrogen, which would bring the calculated nearer to the experimental value.

SUMMARY.

Sulphur hexafluoride, as usually prepared, has been shown to contain carbon fluorides, formed from the graphite anode of the fluorine cell. To obviate this, the fluorine was first passed through liquid oxygen, and sulphur hexafluoride prepared from it was found to be highly pure.

A new sulphur fluoride, disulphur decafluoride, has been isolated in a pure state by an improved method of fractionating small quantities of gases. It has been analysed, and its chemical properties briefly investigated. It is stable, but not so inert as the hexafluoride. Its b. p. is 29°, m. p. — 92°; its liquid density is 2·08 g./c.c., and its surface tension 13·9 dynes/cm., both at 0°. The Trouton constant is 23·0. The parachor is 236, in fair agreement with a sexacovalent structure.

In conclusion we thank Imperial Chemical Industries, Ltd., for a grant which has helped to defray the cost of the research. One of the authors (K. G. D.) also thanks the authorities of Leeds University for an Akroyd and a University Research Scholarship, and also the Trustees of the Wakefield Charities for the grant of a Brotherton Research Scholarship.

LEEDS UNIVERSITY. [*Received, July* 18*th*, 1934.]