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THE PREPARATION OF SULFUR HEXAFLUORIDE AND SOME OF ITS PHYSICAL PROPERTIES

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The object of the present research was to investigate in somewhat greater detail than previously has been described the preparation and purification of sulfur hexafluoride, as well as to determine certain of its physical properties which appeared to be in need of revision. Because of the increasing attention which is being given to certain gaseous fluorides as well as the rather unusual intrinsic characteristics of sulfur hexafluoride, it was thought desirable to communicate the results of our study thus far established. Sulfur hexafluoride is a gas at ordinary temperature; it solidifies at low temperature, melting at −50.8°. Its vapor pressure at that temperature is above atmospheric; it must be cooled further, to −63.8°, to lower the pressure to 760 mm.; the determination of these temperatures and pressures was one of the objects of this work.

The Generation of Fluorine.—The only practical method of preparation of sulfur hexafluoride is the combustion of sulfur in fluorine, so that a brief account of our experience with the generation of fluorine would not appear to be out of place here. Since Moissan's[1] first preparation of this gas by the electrolysis of a solution of potassium fluoride in anhydrous hydrogen fluoride, using a U-tube and electrodes of platinum–iridium, much improvement in the design and operation of fluorine generators has been attained. Of various types of generators, such as those of F. Meyer and Sandow,[2] J. Simons,[3] Lebeau and Damiens,[4] and Bancroft and Jones,[5] that described by the last-named investigators is representative of recent practice. Their generator is an improved form of that first described by W. L. Argo,[6] the essential change being in the use of magnesium metal in place of copper for the containing vessel and diaphragm.

In starting the present work, several types of fluorine generators using fused electrolytes were constructed and the unsuitability of copper for the containing vessel and diaphragm was soon established. The generator finally adopted and successfully operated over an extended period of time was a modification of that described by Bancroft and Jones, with one

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[1] Moissan, *Compt. rend.*, **53**, 202 (1886).

[2] F. Meyer and Sandow, *Ber.*, **54**, 759 (1921).

[3] J. Simons, THIS JOURNAL, **46**, 2175 (1924).

[4] Lebeau and Damiens, *Compt. rend.*, **181**, 917 (1925).

[5] Bancroft and Jones, *Trans. Am. Electrochem. Soc.*, **55**, 71 (1929).

[6] Argo, Mathers, Humiston and Anderson, *J. Phys. Chem.*, **23**, 348 (1919).

important difference: welded 3.2 mm. monel metal was used in place of magnesium in the construction of the vessel and diaphragm. After more than one hundred and fifty hours of operation at 220 to 300° there has been no appreciable attack of the monel by the fused electrolyte—KHF_2— and only a slight attack of the graphite anode.

Electrical connection was made to the graphite anode by means of a 3.2-mm. copper wire threaded at the end and screwed tightly into the 2.54-cm. graphite rod, the whole being held at the top of the diaphragm by a "stopper" of Portland cement. A horizontal copper disk attached to the lead wire served as a shield to prevent spray from entering and clogging the outlet tube. The bottom of the diaphragm was closed with a removable monel disk held snugly to the diaphragm by three flat hooks brazed to the latter. Three rows of eight 6.4 mm. holes perforated the lower end of the diaphragm. The current employed varied from 12 to 15 amp.; the potential drop across the cell averaged 3 to 4 volts. The generator held approximately 3.6 kilos of electrolyte, which was melted in a large copper beaker before pouring into the generator, wherein it was kept molten by means of a nichrome heating coil wound about the vessel. When a run was interrupted, the electrolyte was poured out into the copper beaker, in which it solidified. When the electrolysis was resumed the cake was dislodged, broken into large lumps, remelted and again poured into the generator. The fluorine contains some hydrogen fluoride, oxygen and probably a little carbon tetrafluoride. As far as the satisfactory functioning of the generator is concerned, our experience confirms the observations of others in that the water content of the electrolyte has much to do with successful operation. As electrolysis proceeds—at as low a temperature as possible, in order to minimize vaporization of hydrogen fluoride—the water is gradually eliminated.

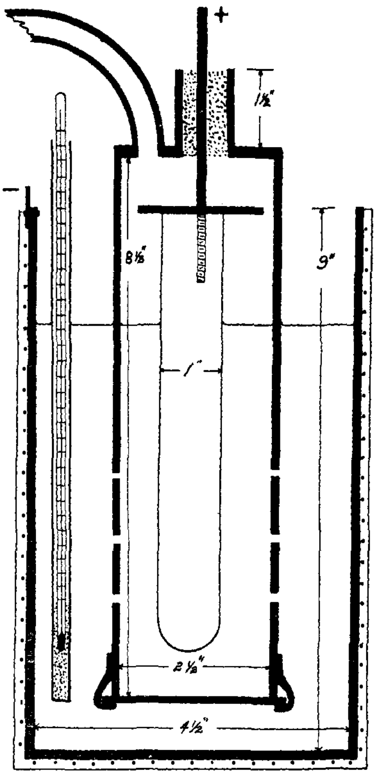

Fig. 1.—Fluorine generator.

The Preparation of Sulfur Hexafluoride and Previous Work.—Moissan and Lebeau[7] discovered that when sulfur burns in fluorine the chief product of the reaction is the gas, sulfur hexafluoride, colorless, odorless and very inert under ordinary conditions. Of this substance they say that "it solidifies at about −55° to a white, crystalline mass, which liquefies and boils at a temperature but little removed from its melting point." In determining the density of the gas, Moissan and Lebeau used a method

[7] Moissan and Lebeau, *Compt. rend.*, **130**, 865 (1900); *Ann. chim. phys.*, [7] **26**, 147 (1902).

previously described by Moissan and Gautier,[8] which consisted of the comparison of the weights of equal volumes of sulfur hexafluoride and of air taken under the same conditions. Four values were given: 4.95, 4.99, 5.09 and 5.11; average 5.03.

Prideaux[9] later made a comparative study of the physical properties of the hexafluorides of sulfur, selenium and tellurium. The sulfur hexafluoride had been purified by three distillations. He determined the melting point of sulfur hexafluoride as −56 to −55°, the boiling point as −62° at 760 mm., and made a determination of the vapor pressure of solid sulfur hexafluoride over the temperature interval −110° to about −65°. The pressure, 760 mm. at −62°, was calculated by a short extrapolation, since there was not enough sulfur hexafluoride to continue the readings to this temperature. The data were not tabulated but were given in the form of a smooth curve. The temperature of the sulfur hexafluoride was assumed to be the same as that of the ether (cooled with liquid air, and gradually allowed to warm up) that surrounded the bulb. The apparatus was quite small because of the small amount of the substance available.

The method of preparation of sulfur hexafluoride used in the present investigation was as follows. The fluorine from the generator passed through two copper U-tubes coupled thereto and filled with flakes of freshly fused potassium fluoride to remove some of the hydrogen fluoride, then through a 2.5-cm. copper tube about 50 cm. long filled with small lumps of sulfur. The sulfur ignites immediately in the fluorine and the progress of the combustion can be noted by the heating of the copper tube at the zone of combustion. The gases from the reaction tube passed through a long column of freshly fused potassium hydroxide flakes to remove the greater part of lower fluorides of sulfur and any sulfur dioxide present. The gas was now collected over 3 *N* potassium hydroxide in a 20-liter carboy, the solution being siphoned out as the carboy filled with gas, and the whole allowed to stand for several days with occasional shaking. From the carboy the gas was passed at a rate of about 1.5 liters per hour through a trap cooled to approximately −60° to remove much of the water vapor, through a column of calcium chloride, and then through two absorption bottles containing anhydrous alcohol. Next the gas passed through two absorption bottles containing water and one containing concentrated sulfuric acid to remove alcohol vapor, and finally was solidified by strong cooling in the first of a series of four bulbs. The quantity of solid so obtained was about 80 g. The solid was now repeatedly sublimed, each operation requiring from five to seven hours and approximately one-third (the first and last portions) of each fraction being discarded. Finally the bulb of the vapor pressure apparatus was well evacuated, cooled with liquid air, and the sulfur hexafluoride sublimed directly into it.[10]

Vapor Pressure of Sulfur Hexafluoride.—The apparatus shown in Fig. 2 was employed in the vapor pressure measurements. The purpose of the compressed air, mercury reservoir and stopcocks attached thereto was to make possible the adjustment of

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[8] Moissan and Lebeau, *Compt. rend.*, **130**, 984 (1900); Moissan and Gautier, *Ann. chim. phys.*, [7] **5**, 568 (1895).

[9] Prideaux, *J. Chem. Soc.*, **89**, 323 (1906).

[10] It was observed that at the temperature of liquid air the vapor pressure of solid sulfur hexafluoride is certainly less than 0.01 mm.

the mercury level in the short arm to the same point when taking readings, so that the work could be carried out at constant volume. The scale was a metal tape, one inch wide, graduated in millimeters. The bulb containing the sulfur hexafluoride was cooled with a mixture of alcohol and solid carbon dioxide in a one-liter Dewar flask. The temperature of this bath was taken as the temperature of the sulfur hexafluoride. This was justifiable for several reasons: (1) the bath in some runs was allowed to warm up very slowly from one point to the next, not less than six hours being taken for a temperature interval of 25°; (2) as will be described presently, the bath could be held at a given temperature for ten or fifteen minutes without further change in pressure; (3) check pressure readings could be obtained with falling temperature. The bath was kept well stirred throughout by means of a motor-driven stirrer. By the gradual addition of cold alcohol–carbon dioxide mixture to the bath it was possible to keep the temperature constant (within approximately 0.1°), or by regulating the rate of addition, to lower the temperature stepwise and thus reach equilibrium from the upper side.

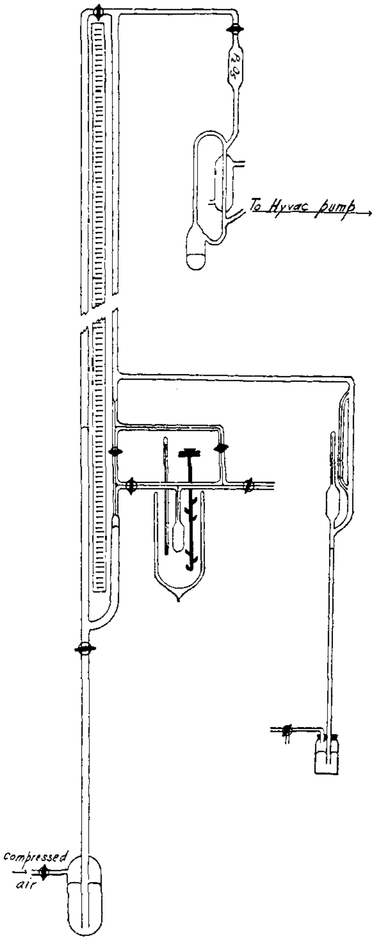

Fig. 2.

Seven runs were made on the vapor pressure, the results of which are shown in the accompanying table and graph. The values designated as "Experimental Data" in the table represent, in general, the mean of several determinations at the given temperatures; from these results the smooth curve was constructed, and from the graph, in turn, the interpolated values given in the table were obtained. By interpolation, likewise, the temperature at which the vapor pressure of solid sulfur hexafluoride becomes 760 mm. was found to be −63.8°. In the individual runs a check upon the purity of the substance was obtained by permitting successive fractions of the same to vaporize, measurements being taken before and after the vaporization. In three runs, beginning with the solid at the lowest temperature (about −72°), the vapor pressure readings were made at intervals with very slowly rising temperature, and were extended well above the melting point (−50.8°); readings were then taken while the substance was cooled slowly, thus passing from the liquid to the solid state. Further evidence of the purity of the substance is afforded by the fact that the measurements recorded were made upon two entirely different samples of sulfur hexafluoride, independently prepared and purified.[11]

TABLE I

VAPOR PRESSURE OF SULFUR HEXAFLUORIDE

Experimental data				Interpolated from graph	
Temp., °C.	Press., mm.	Temp., °C.	Press., mm.	Temp., °C.	Press., mm.
−72.4	433	−58.3	1081	−72.0	445
−71.4	460	−57.5	1141	−70.0	506
−70.9	471	−56.0	1248	−68.0	578
−69.1	535	−54.8	1335	−66.0	660
−67.8	588	−53.1	1472	−64.0	749
−67.0	628	−52.0	1581	−62.0	849
−66.6	635	−51.1	1655	−60.0	966
−65.5	686	−50.1	1745	−58.0	1099
−64.4	734	−49.7	1772	−56.0	1247
−63.8	766	−49.1	1834	−54.0	1405
−62.5	827	−47.8	1928	−52.0	1577
−61.7	867	−46.8	2007	−51.0	1675
−60.8	921	−46.4	2054	−50.0	1745
−59.8	976			−49.0	1820
				−48.0	1892
				−47.0	1987
				−46.0	2090

Melting Point of Sulfur Hexafluoride.—The melting point of sulfur hexafluoride as given by Moissan is −55° and by Prideaux −56 to −55°. This value could not be checked by us either from the interpretation of the vapor pressure curves or by direct observation of the melting and solidification of a small quantity of the substance contained in a sealed bulb. The melting point of our purified product thus observed was found to be −50.8 ±0.2°, this value being checked repeatedly. The melting point as indicated by the break in the vapor pressure curve is in fair agreement with this value, but inasmuch as the change of slope at the triple point is so slight, the precise location of the break in the curve is uncertain. Consequently, the value given is based mainly upon the result of direct observation of the melting point. The low values of the earlier observers we feel were due to the presence of impurities. This is also reflected in the case of the gas density determinations which follow.

Density of Gaseous Sulfur Hexafluoride.—The density of gaseous sulfur hexafluoride was determined at 20.0°, using the purified material employed in the vapor pressure work. The density globe of known weight and internal volume (495.56 cc.) was connected to the sulfur hexafluoride bulb, the latter immersed in liquid air, and the system evacuated to less

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[11] It may be worth noting that the pressure of the gas at room temperature becomes too great for ordinary glass apparatus, but there is no reason why liquid sulfur hexafluoride may not conveniently be stored in metal cylinders; the equilibrium pressure under ordinary conditions probably would not exceed greatly that of liquid ammonia.

than 0.001 mm. By allowing the sulfur hexafluoride to warm up the density globe was permitted to fill with the gas at a pressure of a little more than atmospheric. The globe was then removed and placed in a thermostat at 20.0° where it remained for at least fifteen minutes; the stopcock was then opened momentarily to bring the gas to atmospheric pressure and after another short interval again opened and closed, the barometer reading now being taken. The globe and sulfur hexafluoride were weighed by the counterpoise method, employing the usual precautions. The external volumes of counterpoise and globe differed by not more than 0.5 cc. The results given are corrected for the change in volume of the density globe on evacuation, and the pressures refer to mercury at 0°. For the sake of comparison with Moissan's determinations, the relative density referred to air is also given, calculated by assuming the average molal weight of air to be 28.98 and that sulfur hexafluoride behaves as a perfect gas over the interval involved. The theoretical value for sulfur hexafluoride is 5.04.

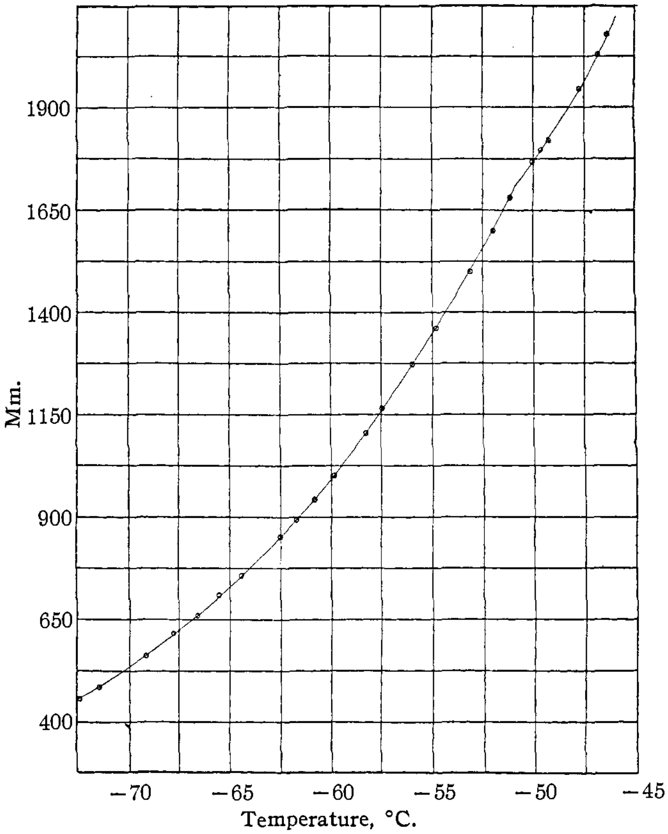

Fig. 3.—Vapor pressure of sulfur hexafluoride.

	Pressure, mm.	Density, g./liter at 20.0°	Relative density (air = 1)
I	753.5	6.091_7	5.10_1
II	753.5	6.094_9	5.10_3
III	760.5	6.164_6	5.11_4
			5.10_6 (mean)

Summary

1. In the preparation of fluorine, monel metal has been found entirely satisfactory for the cathode vessel and diaphragm in the electrolysis of fused potassium bifluoride. Graphite as the anode material is slightly attacked. Details concerning structural features and operation of the fluorine generator are given.

2. The synthesis and purification of sulfur hexafluoride are described; the method of purification is more complete than hitherto has been described.

3. The vapor pressure of solid and liquid sulfur hexafluoride has been measured up to three atmospheres, the temperature interval covered being from −72 to −45°. The pressure becomes 760 mm. at −63.8°.

4. The density of the gas at 20°, 753.5 mm., is found to be 6.093 g. per liter. From this the relative density (air = 1) is calculated to be 5.10_6; theoretical, 5.04.

5. The melting point of pure sulfur hexafluoride is found to be −50.8 ± 0.2°. This is more than 4° higher than the earlier values of Moissan and of Prideaux.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

DEFORMATION OF ELECTRON SHELLS. II. ABSORPTION SPECTRUM, MOLECULAR VOLUME AND REFRACTION OF CERTAIN RARE EARTH SALTS

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In the first paper of this series[1] it was pointed out that there is a relation between the absorption spectrum and other properties of neodymium perchlorate. The object of the present work was to extend the observations to the nitrate and chloride of neodymium and, so far as possible, to other members of the rare earth group.

Experimental

The experimental procedure involved in the measurements described here will be given only wherein it differs from that already reported.

The quantitative analysis of neodymium nitrate solutions presented a

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[1] Selwood, THIS JOURNAL, 52, 3112 (1930).