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The Thermochemical Constants of the Hexafluorides of Sulfur, Selenium and Tellurium

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Introduction

The hexafluorides of the elements of the sulfur group are of interest because of the uniformity of their physical properties, their comparative unreactivity, and the fact that in these compounds sulfur, selenium and tellurium exhibit their maximum valence of six. All three substances are gases at ordinary temperatures, they sublime before melting, and, with the exception of tellurium hexafluoride, they do not hydrolyze in the presence of water.

Aside from the earlier work of Moissan[1] and of Prideaux,[2] no further investigations of the hexafluorides of selenium and tellurium appear to have been carried out, and in their investigations no careful attempt was made to purify the substances prepared. Schumb and Gamble[3] have carried out a careful study of the preparation and physical properties of sulfur hexafluoride and their results are presented below for purposes of comparison. No determinations of the heats of formation of any of these three compounds seem to have been made.

In addition to the hexafluorides small quantities of liquid lower fluorides are formed when fluorine reacts with the elements of the sulfur group and, with the exception of sulfur tetrafluoride,[4] these substances have not previously been observed.

In this article are presented the results of experiments on the preparation and physical and chemical properties of selenium and tellurium hexafluorides and the values obtained for the heats of formation of sulfur, selenium and tellurium hexafluorides. Results of experiments on a lower fluoride of tellurium are also included.

Preparation and Purification of the Hexafluorides.—The hexafluorides were prepared by passing fluorine gas from a generator over the elementary substances contained in a copper tube. The reaction in all cases took place without any major disturbances such as explosions or extensive attack on the copper container. The fluorine was generated at the rate of about one and one-half liters per hour, the generator being of the conventional type using fused potassium acid fluoride as the electrolyte. The current efficiency was about 30%. The substances prepared were collected in *Pyrex* glass traps cooled with a carbon dioxide–alcohol

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(1) Moissan, *Ann. chim. phys.*, [7] **27**, 145 (1902).

(2) Prideaux, *J. Chem. Soc.*, **89**, 323 (1905).

(3) Schumb and Gamble, THIS JOURNAL, **52**, 4302 (1930).

(4) Fischer and Jaenckner, *Z. angew. Chem.*, **42**, 810 (1929).

mixture. Hydrogen fluoride was effectively removed by causing the gas from the generator to pass through a copper tube containing anhydrous sodium fluoride.

The resulting material was purified by means of a series of fractional sublimations carried out in highly evacuated containers, liquid air being used to remove the more volatile products, and alcohol cooled with carbon dioxide served to fractionate what remained. The substances were caused to melt between the sublimation operations. Very little highly volatile product was obtained and only in the case of tellurium were appreciable quantities of a much less volatile substance found. The test for purity was the constancy of the freezing point and the vapor density of the substance being purified.

Experimental Methods

The vapor densities were determined by means of a liter flask equipped with an all-glass click-gage for measuring the pressure, and a standardized thermometer graduated in tenths of a degree served for the temperature measurements.

The apparatus used for the vapor pressure measurements consisted of an all-glass click-gage to which a glass container was attached by means of small-bore tubing. The container was surrounded by a well stirred alcohol-bath cooled with carbon dioxide or liquid air, and the click-gage was outside of this bath with its temperature that of the room. The bath temperature was measured with a thermocouple calibrated at the solid carbon dioxide and melting mercury points. No pressure measurements were made until variations of the temperature by ±0.1° caused a corresponding change in the pressure.

All melting points were determined separately and are believed to be correct to within ±0.1°.

The calorimeter for determining the heats of formation of the three hexafluorides consisted of a two-liter Dewar flask surrounded by a thick layer of insulating material and equipped with a tight insulating cover. It was provided with an electrically operated stirrer, an electric heating coil for determining its heat capacity and a Beckmann thermometer, and contained from 1.2 to 1.4 liters of distilled water. A hollow cylindrical copper tube 2.5 cm. in diameter and length and provided with a threaded copper plug was employed as a reaction cell. A rubber gasket rendered the threaded joint water and gas tight and the threads, after screwing the plug firmly into the cell, prevented any appreciable diffusion of the fluorine to the gasket. Two small copper tubes attached to the cell and passing through the cover of the calorimeter were used for introducing the fluorine and removing the hexafluoride formed, the exhaust tube being coiled near the reaction cell to facilitate complete heat transfer.

A deep platinum dish placed in the reaction cell was used to hold the solid reactants, and it was found that neither the fluorine nor the sulfur group elements had any appreciable effect on the platinum. A copper dish was used in some preliminary experiments but it was found to be attacked by sulfur during the course of the reaction with fluorine. The only losses of solid material were the result of vaporization to the copper walls of the cell and were estimated qualitatively as a few tenths of a milligram. The weights of material used in the runs varied from 0.2000 g. to 0.4000 g. and the temperature rise varied from about 0.750 to 1.100°. A satisfactory run occupied about fifteen minutes and the same length of time was employed in determining the heat capacity of the calorimeter. Blank runs made with no reactant in the cell showed that no appreciable amount of reaction took place between the fluorine and the copper.

The errors involved in the vapor pressure measurements vary from ±0.2 mm. at the lowest pressures to ±2.0 mm. at the highest. The individual values for the heats of reaction showed deviations from the mean of 1.5% in the case of sulfur, 0.7% for selenium and 0.3% for tellurium. It is believed that the final results given are reliable to within 2%. More refined measurements will certainly necessitate the use of an all-platinum reaction cell to reduce to a minimum the errors due to the small losses by evaporation to the walls of the cell. The eventual loss in heat liberated appears to be due to the unreactivity of the fluorine toward the copper sulfide formed.

Results of the Experiments

In Tables I and II are presented the results of the vapor pressure and vapor density measurements.[5] The vapor pressure equations constructed from the experimental data are given in Table III. Table IV contains the thermochemical constants for the three hexafluorides as determined directly or calculated from the vapor pressure measurements. The values given

TABLE I

THE VAPOR PRESSURES OF SOLID SeF_6

Temp., °C.	Pressure, mm.
−48.7	651.2
53.8	469.3
59.4	318.4
64.8	213.1
69.3	147.9
77.9	72.1
84.4	43.3
87.5	30.4

Molecular wt., exptl., 191.3
Formula wt., calcd., 193.0

TABLE II

THE VAPOR PRESSURES OF SOLID TeF_6

Temp., °C.	Pressure, mm.
−40.1	695.1
45.6	501.6
50.0	361.3
55.7	246.6
60.3	182.5
65.3	122.2
68.4	94.1
74.7	53.4
75.4	48.4
78.8	29.4

Molecular wt., exptl., 240.9
Formula wt., calcd., 241.5

TABLE III

VAPOR PRESSURE EQUATIONS OF SOLID SULFUR, SELENIUM AND TELLURIUM HEXAFLUORIDES

$$SF_6(s) \quad \log_{10} p_{\text{mm.}} = (-1231.3/T) + 8.7648$$
$$SeF_6(s) \quad \log_{10} p_{\text{mm.}} = (-1440.8/T) + 9.2417$$
$$TeF_6(s) \quad \log_{10} p_{\text{mm.}} = (-1471.4/T) + 9.1605$$

TABLE IV

THERMOCHEMICAL CONSTANTS OF THE HEXAFLUORIDES OF SULFUR, SELENIUM AND TELLURIUM

Subs.	Heat of formation of gas, cal.	Heat of sublimation of solid, cal.	Heat of fusion of solid, cal.	M. p., °C.	Sublimation point, °C.
SF_6	262,000	5640	1390	−50.8	−63.8
SeF_6	246,000	6600	(2010)	−34.6	−46.6
TeF_6	315,000	6740	(1900)	−37.8	−38.9

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(5) The recently published values for the vapor pressures of selenium and tellurium hexafluoride by Klemm and Henkel [*Z. anorg. allgem. Chem.*, **207**, 73 (1932)] are, at the lower temperatures, higher than those presented here. The difference appears to result from the fouling of the mercury in their manometer, and they call attention to this difficulty. This source of error has been avoided in our measurements by the use of the all-glass click-gage.

for sulfur hexafluoride, with the exception of its heat of formation, were obtained using the data of Schumb and Gamble.[3]

The values for the heats of fusion of selenium and tellurium hexafluorides, given in parentheses, were calculated from the heats of vaporization of the liquids which were obtained by an application of Trouton's rule to estimates of the boiling points using the known values for sulfur hexafluoride to determine the necessary constant. Since the melting point of tellurium hexafluoride is only 1.1° above the sublimation point, the value for the heat of fusion cannot be in error by much more than 10 cal. The corresponding value for selenium hexafluoride may be in error by 50 cal.

All three hexafluorides have a vapor pressure of one atmosphere before the melting point is reached. The solid selenium hexafluoride, when condensed at the temperature of solid carbon dioxide–alcohol mixtures, forms a clear ice-like solid while the corresponding tellurium compound forms a white mass of small crystals.

A second modification of the tellurium compound appears to form at $-73.5°$ since at this point a discontinuity in the log p–$1/T$ curve is observed.

The values obtained for the melting points differ appreciably from those obtained by Prideaux. The same lack of agreement was found by Schumb and Gamble in the case of the sulfur compound and is discussed more fully in their paper. Both lack of purity and the thermometer used are the obvious reasons for the differences.

Discussion of the Results

As may be seen by comparing the sublimation and melting points, the three hexafluorides are very similar in their physical properties. That the thermal constants do not vary uniformly as one proceeds from sulfur to tellurium, may be seen from the melting points, that of selenium hexafluoride being higher than either of those for sulfur or tellurium. Also the heats of formation show this reversal markedly, the values being in an order different from the melting points. The heats of fusion are in the same order as the melting points.

These reversals of order from the positions in the periodic table are to be found in the heats of formation of the dioxides as well, the order being the same as the heats of formation of the hexafluorides.

Experiments on the Reactivity of Selenium and Tellurium Hexafluorides

It is known from the experiments of Prideaux[2] that sulfur and selenium hexafluorides do not react with water while the tellurium compound does so slowly. Further experiments of a qualitative nature were carried out to determine if this relative inertness could be observed in other reactions.

A bulb containing selenium hexafluoride and elementary selenium was heated and observed for evidence of any reaction. No effect was noted until the glass was so hot that it began to melt, and at that point white fumes were noted. It was not possible to determine whether the reaction involved the selenium or only the glass.

The corresponding experiment in which tellurium hexafluoride and tellurium were used showed signs of reaction at much lower temperatures, dense white fumes developing when the temperature was, locally, not much above 200°. A white solid, presumably tellurium difluoride, separated in considerable amounts.

Two tubes were filled with mixtures of selenium hexafluoride and ammonia gas, the two gases having approximately the same partial pressures. One tube was placed in an electric furnace and the temperature gradually raised; at 200° traces of elementary selenium were observed; at higher temperatures the reaction proceeds somewhat more rapidly. The second tube was placed in the furnace at 330° and selenium was observed to form in increasing amounts over a period of five minutes. On breaking under water and testing the resulting solution for fluoride, an appreciable precipitate of calcium fluoride was obtained, though not as large as would be expected if no loss of detectable fluoride had occurred. The loss was due, doubtless, to the reaction of the hydrogen fluoride formed with the glass.

If Ruff's[6] value of 64,000 cal. for the heat of formation of hydrogen fluoride is used in connection with the value 11,000 cal. for ammonia and the value given in Table IV for selenium hexafluoride, then the reaction

$$2NH_3(g) + SeF_2(g) = N_2 + Se + 6HF + 116{,}000 \text{ cal.}$$

is found to take place with a large evolution of heat. The fact that the reaction does take place shows that the entropy change is not sufficiently great to make the free energy and change in heat content of opposite signs. The entropy change is doubtless such that the reaction has a very great tendency to take place over a rather large temperature range. The entropy of selenium hexafluoride would have to be about 700 cal./deg. to make $\Delta F^\circ = 0$ and such a value is quite certain to be several times greater than the true one. Similar considerations indicate that sulfur and tellurium hexafluorides would also be reduced by ammonia or hydrogen and that sulfur hexafluoride is not to be expected as the result of a reaction between solutions of sulfuric and hydrofluoric acids. It is seen therefore that the inertness of the hexafluorides toward reducing agents cannot always be ascribed to a lack of thermodynamic tendency to react.[7]

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(6) Ruff, *Z. anorg. allgem. Chem.*, **198**, 375 (1931).

(7) The results of recent electron diffraction experiments by Pauling and Brockway (private communication) show that the fluorine atoms in the hexafluorides lie at the corners of a regular tetrahedron. For sulfur hexafluoride they find the S–F distance to be 1.58 Å. From this result the entropy of sulfur hexafluoride at 25° and 1 atm. was calculated to be 62 cal./deg. It was assumed, as seems reasonable, that the vibrational entropy is small. Using this value together with the entropy of solid sulfur, 7.6 cal./deg. and fluorine 48.04 cal./deg., and the heat of formation given above, we find for

$$S(s) + 3F_2(g) = SF_6(g) \quad \Delta F^\circ_{298} = -235{,}000 \text{ cal.}$$

It is now easy to show that sulfur hexafluoride should be completely hydrolyzed by water vapor at 25° to give sulfur trioxide and hydrogen fluoride.

The Lower Volatile Fluorides of Selenium and Tellurium.—During the preparation of selenium hexafluoride a colorless liquid was observed to condense out in the train before reaching the cold traps. It was collected in a tube and the tube sealed off and set aside. On the following day the tube was found to be shattered and the fragments covered with small amounts of selenium. The liquid was evidently some lower fluoride which decomposed to form the more volatile hexafluoride and selenium or a still lower fluoride.

In the case of tellurium the purification by fractionating yielded about 1.3 cc. of a colorless liquid residue much less volatile than the hexafluoride. This residue was further fractionated and about 1 cc. of liquid obtained which was distilled under vacuum into a tube equipped with a click-gage and a series of small side tubes. After freezing with liquid air and sealing off the original container, the tube containing the liquid was surrounded by a bath of finely divided melting ice. The vapor pressure was then measured, a portion of the liquid distilled into a side tube, and the side tube sealed off. Both the side tube and main tube were cooled with liquid air before sealing to avoid the decomposition which results when the vapor is in contact with hot glass. This process was repeated until all the material had been thus distilled into seven small tubes.

The vapor pressures at 0.0° varied from 81.4 mm. for the original amount of liquid to 27.6 mm. for the last portion, thus showing that a pure product had not been obtained. The vapor densities of the second and sixth portions were determined and the results gave molecular weights of 342.0 and 341.6, respectively, showing that the composition had varied but little as a result of the fractionation. The melting point of the first fraction was found to be $-13.6°$ and the boiling point 61.2°. An attempt was made to analyze the material for tellurium and fluorine but no precise results were obtained due to the difficulties involved. The method of preparation renders the presence of oxygen in the substance very unlikely.

Conclusions as to the nature of the substance must be based principally on the vapor density results. No tellurium fluoride molecule containing only one atom of tellurium would have a molecular weight as high as 342, since the molecular weight of TeF_6 is only 241.5. The compounds Te_2F_8 and Te_2F_6 would have as molecular weights 407.0 and 369.0, respectively, while Te_2F_2 and Te_2F_4 would have values lower than the observed one, namely, 293.0 and 331.0, respectively. From the results it is not possible to give the exact composition of the liquid material. It appears to be a mixture of two or more compounds and at least one of them contains more than one atom of tellurium in the molecule, but the formulas for these compounds cannot be given with certainty at this time.

When the liquid, enclosed in a glass tube, is placed in hot water (85° or greater), a fairly rapid decomposition takes place with the formation of a white precipitate which is presumably the difluoride. The liquid is denser than water and reacts slowly with it with the evolution of a small amount of gas, the gas in turn reacting slowly with the water in much the same manner as does the hexafluoride.

The small amount of material obtainable makes a more extensive study of the compound not feasible at this time.

Summary

The vapor pressures, melting points and sublimation points of selenium and tellurium hexafluorides have been measured and determinations of the heats of formation of the hexafluorides of sulfur, selenium and tellurium have been made. The resulting thermochemical constants of the three compounds have been calculated and presented in Table IV.

It has been found that selenium hexafluoride reacts with ammonia gas slowly at 200° and much more rapidly at 330°, to give selenium, nitrogen and hydrogen fluoride. This fact together with the thermal data has been used to show that the inertness of the hexafluorides toward reducing agents is not to be ascribed to a lack of thermodynamic tendency to react.

A lower liquid fluoride of tellurium has been discovered.

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Studies on Oxidation-Reduction. XVIII. Simple Safranines

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Preliminary measurements in three laboratories[1] have assigned to certain dyes of the azine group potentials which are much lower than those which characterize any indicator system discussed in the first sixteen papers of this series. For this reason azine dyes have been used in several attempts to reveal the extreme reducing ability of cells in anaerobiosis, and they have been considered as possible mediators for the potentiometric study at low potentials of "electromotively inactive" systems. However, the precision of none of the preliminary physical measurements was satisfactory and the conduct of the reductants led Cohen, Chambers and Reznikoff[2] to doubt their usefulness in the biological field. Therefore we have reexamined a few of the simpler safranines.

The potential measurements which we now report are good criteria of the primary reversibility of the oxidation–reduction process. They define

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(1) Clark and Zoller, *Science*, **54**, 557 (1921); Vellinger, *Arch. phys. biol.*, **7**, 113 (1929); Rapkine, Struyk and Wurmser, *J. chim. phys.*, **26**, 340 (1929).

(2) Cohen, Chambers and Reznikoff, *J. Gen. Physiol.*, **11**, 585 (1928).