UNCLASSIFIED

~~CONFIDENTIAL~~

Report A-83

~~SECRET~~

SECURITY INFORMATION

CHEMICAL PROPERTIES OF URANIUM HEXAFLUORIDE, UF_6

By

Aristid V. Grosse

* * * * * *

CLASSIFICATION CANCELLED
DATE 7/20/60 tc
For The Atomic Energy Commission
H. F. Carroll
Chief, Declassification Branch

~~"This material contains information affecting the national defense of the United States within the meaning of the espionage laws, Title 18, U.S.C., Secs 793 and 794, the transmission or revelation of which in any manner to an unauthorized person is prohibited by law."~~

Thi[redacted] fill your request ~~as our~~ sup- ply of copies was exhausted. [redacted] need [redacted] files, [redacted] is so T[redacted] used to fill future requests ~~from~~ other AEC ~~installations.~~

~~RESTRICTED DATA~~

~~This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.~~

This document is
PUBLICLY RELEASABLE
Hugh Kinser
Authorizing Official
Date: 8/21/09

SECURITY INFORMATION

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

147 1

~~SECRET~~

UNCLASSIFIED

DISCLAIMER

~~SECRET~~ UNCLASSIFIED

~~CONFIDENTIAL~~

TABLE OF CONTENTS

This document c[redacted]formation affecting the national defense of the United States within the meaning of the Espionage Act, U S C 50; and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

UNCLASSIFIED ~~SECRET~~

~~CONFIDENTIAL~~ ~~SECRET~~

CHEMICAL PROPERTIES OF URANIUM HEXAFLUORIDE, UF_6

By

Aristid V. Grosse, Department of Physics and
Chemistry, Columbia University, New York, N. Y.
June 25, 1941

Uranium hexafluoride has the distinction of being the only stable gaseous compound of uranium known up to the present moment. Because of this property it is the only compound that can be used for processes of isotope separation, such as diffusion, thermal diffusion, centrifuge separation, distillation, and others of a similar nature.

(At this point it might be worth while to emphasize that there may be possibilities of preparing other volatile uranium compounds, such as, for instance, uranium carbonyl or some alkyl uranium derivatives, or even as a distinct possibility, some mixed alkyl carbonyls of uranium).

Uranium hexafluoride was discovered by Otto Ruff and A. Heinzelmann,[1] in 1909, in Germany, and practically all information published on this compound is found in the German journals. All literature references (1-5) on UF_6 are given at the end of this report.

Summaries on the properties of this compound may be found in Mellor's Treatise, Vol. XII, p. 75-76 (1932), and also in Gmelin's Handbook System No. 55, p. 121-123 (1935), and Abegg's Handbook Vol. IV, 1, 11, p. 930-932 (1921). It is assumed that all data in these reference books are known to the reader. Therefore in this report only substantially new

[illegible]SIFIED

data will be discussed in detail and old data only commented upon or criticized in the light of new facts.

The following short description of the properties of UF_6 is intended for a reader interested only casually in this compound:

UF_6 is a very reactive compound and a very strong fluorinating agent. It is immediately hydrolized by water: In fluorinating reactions it is reduced to the green highly stable UF_4. It reacts instantaneously with hydrogen at room temperature. It fluorinates many metals; sodium and mercury are attacked in the cold, lead, zinc, tin and iron on heating; platinum and gold react only above 400°C. With organic compounds like alcohol, ether, benzene or toluene, immediate fluorination takes place with formation of HF and carbon or carbonaceous material.

The compound forms colorless, very volatile, beautiful transparent crystals of high refractive index. Melting point = 69.5°; boiling point at 760 mm= 56.2°; $D_{20°}$=4.68. The crystals melt under pressure to a transparent colorless liquid of high density, but great mobility.

The present writer had occasion to study this interesting compound when he prepared it for F. W. Aston's(1) first successful isotopic analysis of uranium in 1931. This report covers his investigations carried out intermittently and in a preliminary way at the Department of Physics of

---

(1) Nature 128, 725 (1931).

Columbia University from December, 1939, to date.

This report is divided into the following sections:

A. Methods of preparation. Experimental procedure.

B. Exchange reaction of UF_6 and UF_4.

C. Thermal stability of UF_6.

D. Behavior of UF_6 toward inorganic compounds.

E. Behavior of UF_6 toward organic compounds.

F. Handling of UF_6 in glass vessels in the presence of getters.

A. Methods of Preparation.

Otto Ruff[1, 2,] used the following two successful methods of preparation:

a. From metallic uranium and elementary fluorine, according to:

$$U+3F_2 \rightarrow UF_6$$

b. From uranium pentachloride and fluorine, following the reaction:

$$2UCl_5+6F_2 \rightarrow 2UF_6+5Cl_2$$

The first method (a) is the one later used by all other investigators. It has been recently very substantially improved by Dr. P. Abelson at the Bureau of Standards in Washington, by using uranium tetrafluoride instead of uranium metal, in accordance with the equation:

$$UF_4+F_2 \rightarrow UF_6.$$

In this way the consumption of fluorine has been reduced by two-thirds and the costly metallic uranium completely eliminated. Methods of preparing uranium tetrafluoride are simple and fully described in the literature. Additional new data are contained in a report of this writer to Dr. Lyman J. Briggs, (Bureau of Standards, Washington, D. C.).

Ruff[2] also used a third method of preparation which he abandoned, however, because of difficulties encountered and which, if successful would avoid the use of either elementary fluorine or metallic uranium. It consists in the reaction:

$$UCL_5+(5+x)HF \longrightarrow [UF_5]\ xHF\ 5HCl \quad \ldots\ldots \qquad \underline{1}$$

The compound $[UF_5]$ xHF is supposed to decompose on heating into UF_6 and UF_4 and xHF. (Additional data on the properties of pure UF_5 are given on p. 10 and 11). The difficulty Ruff encountered was in the separation of UF_6 from HF.

We have found that the separation of these two compounds can be readily accomplished by fractional distillation in copper apparatus, either in vacuum or a superatmospheric pressures. A preliminary separation of these two compounds can even be accomplished by simple decantation, since we found that UF_6 is only sparingly soluble in anhydrous hydrogen fluoride. Although the first part of the method has not been thoroughly tested at Columbia, the indications are that it might compete with a method using elementary fluorine since anhydrous hydrogen fluoride is now readily available in large quantities on the market and the technical preparation of UCl_5 should offer no greater difficulties than the similar preparation of such chlorides as $AlCl_3$,

$TiCl_4$ or $ZrCl_4$. (Additional data on the properties of pure UF_6 are given on p. 10).

The UF_6 used in our experiments came mainly from the following two sources: The Naval Research Laboratories and the Bureau of Standards in Washington, D. C.

Experimental Procedure

The UF_6 was handled either in glass or copper apparatus. Glass was used when it was desirable to see any possible reaction, and when low pressures were used. The usual type of high vacuum pyrex glass equipment was used. A high vacuum oil pump as a source of vacuum was employed. The connections to any copper tubes were made with duprene tubing. After filling the reaction tubes were usually sealed. In the presence of getters as described on p. 15 of this report, it was possible to handle even liquid UF_6 very nicely.

An all copper apparatus, consisting of receivers, tubes and brass valves and gauges were used when presence of glass was undesirable or when reactions were carried out at higher pressures.

The standard refrigeration industry's brass and copper connections was found to be very practical.

B. Exchange Reaction between UF_6 and UF_4.

A method for exchanging uranium atoms in UF_6, according to the reaction:

$$UF_6 + U^*F_4 \dashrightarrow U^*F_6 + UF_4$$

was desirable in order to replenish the amount of U^{235} in UF_6 samples after their normal content of U^{235} has been exhausted through isotope separation.

UF_4 can be easily prepared on an industrial scale by precipitation of uranous salt solutions with fluorine ion.

We prepared UF_4 by dehydrating the crystalline hydrate $2UF_4,5H_2O$. The latter is a new compound described by the writer in a report to Dr. Lyman J. Briggs. In this way a porous and reactive, anyhydrous tetrafluoride is obtained.

Instead of using U^{235} we used U^{239} as a tracer and employed the usual radioactive indicator technique. Strong sources of this isotope were kindly supplied by Prof. E. O. Lawrence of Berkeley, Calif. U^{239} has a half-life of about 7 days and allows one to work leisurely. It was a very soft β-radiation and was purified when necessary from UX. Of course, at first it was purified from all fission products. The β-ray absorption in Al of most preparations were measured; since we also measured the absorption of both pure U^{239} and UX we could correct for any UX content.

The exchange reaction follows a monomolecular kinetic law as expressed by the equation:

$$K \cdot t = -\log(R_t - R_\infty),$$

where K is the rate constant and R_t and R_∞ the ratio of U^{239}/U^{238} at the tire t and at equilibrium, respectively. The half-time, τ is, of course, expressed by the relation

$$\tau = \frac{\log 2}{K}$$

ASSIFIED

The exchange reaction was carried out in copper containers, under the vapor pressure of UF_6, corresponding to the temperature used.

The UF_4 contained the U^{239}. A weighed amount of the tetrafluoride was placed in the container, the latter evacuated and a known amount of pure UF_6 distilled on to it. In some experiments catalysts were added to the UF_4.

The following are the results obtained:

1. The exchange takes place already at 100°C, between liquid UF_6 and solid UF_4. The half-time is about 360 hours.

2. The rate of exchange can be stepped up by means of catalysis. For instance, small amounts of $HgCl_2$ bring the half time at 100°C down to about 40 hours.

3. The exchange is slow at 100°C because of the formation of the solid UF_5 (see p. 10 and 11). At the temperatures of its decomposition, i.e. about 250-350°C, the exchange can be made much more rapid. It might be advantageous to work just below the critical temperature of UF_6, although this point will have to be decided by future experiments.

C. Thermal Stability of UF_6.

In the course of a study with Dr. E. Booth, of the thermal diffusion method of U-isotope separation, it became desirable to obtain data on the thermal stability of UF_6.

It was soon found that platinum and gold, the most inert materials known, were readily attacked at temperatures above 400°C. At the same time the experimental evidence seemed to indicate that this attack was not due to any free fluorine produced by the breakdown of UF_6, but was rather due to the inherent reactivity of platinum or gold. Due to the volatility of platinum or gold fluorides at the experimental conditions, a fresh metallic surface is continuously produced. Using metals producing non-volatile fluorides such as copper (Melt. P. of CuF - 908°C) and particularly nickel (Melt. Point of NiF_2 = > 1000°) we were able to heat UF_6 up to 550°C with only negligible decomposition.

Our experimental results were as follows:

1. Copper. Gaseous UF_6, at a pressure of 1/2 atmosphere, was heated in a pure copper tube to 520-535°C for 17 hours. The decomposition of UF_6 was less than 0.3 mg UF_6 per cm^2 of Cu-surface and per hour.

2. Nickel. A similar experiment in a pure nickel tube (from the International Nickel Co.), carried out at 1/2 atmospheres and at 515-545°C for 21 hours showed a decomposition of less than 0.001 mg/per cm^2 of Ni-surface and per hour.

It is likely that the slight decomposition noticed is due to the fresh metallic surface at the beginning of the experiment and also to catalysis by the fluorides of U (UF_4) and Cu or Ni, respectively. It is probable that using perfectly non-catalytic material one will be able to use still higher temperatures before decomposition of UF_6 sets in.

Molten CaF_2 or BaF_2 were considered likely non-catalytic material and excellent tubes from both fluorides were kindly prepared by Professors W. Schumb and Gamble of Massachusetts Institute of Technology, Cambridge, Mass. However, to date no experiments were made with them.

All our data under this heading were passed on to Prof. A. O. Nier of the University of Minnesota for use in his Clusius column experiments.

D. Behavior of UF_6 toward Inorganic Compounds

a. Behavior toward metals.

We have found that nickel is the most inert metal, followed by copper, as has been mentioned on p. 8. Iron and its different alloys vary in resistance to quite a degree and are inferior to copper. Usually nickel and chromium containing alloys such as the stainless steels, are very much more resistant than ordinary steel. Metals like zinc and lead are very readily attacked.

Data recently obtained by Dr. P. H. Abelson of the National Bureau of Standards are given in the appendix (see p. 19.)

The following experiments contain some new quantitative data:

b. Copper.

A copper tube containing liquid UF_6 was heated for

100 hours to 100 to 110°C. At the end of this period the tube was opened; it showed a bright red copper surface with no visible deposit of either Cu or U-fluorides under the microscope. The brass valves used on both ends of the tube also showed no visible deterioration.

Experiments with gaseous UF_6 at high temperatures are described on p. 8.

c. Nickel and UF_6. (See p. 8).

In both high temperature experiments the copper and nickel surfaces were covered with their respective fluorides which seemed to adhere very firmly to the surface of the metal and prevented any further corrosion of the metal. While these experiments show a slow rate of reaction of copper and nickel, they are also of interest in demonstrating the high thermal stability of UF_6.

d. Stainless steel.

Stainless steel in the form of Stedman packing was found to be unaffected by liquid UF_6 at 100° for a period of about 24 hours. It is noteworthy that the wires are wetted by UF_6, but the liquid film is very thin because of its high density.

e. Platinum.

A platinum wire mounted in a regular electric bulb fashion in an atmosphere of UF_6 decomposed the latter at a temperature of about 600° fairly rapidly, giving a green deposit of UF_4 and a volatile brown deposit containing platinum, which probably was PtF_4. Comparative experiments with copper and nickel wires show that platnium is much more readily corroded than metals like nickel and copper, which are protected by the already mentioned (p. 8) films of non-volatile fluorides. As has been demonstrated by Ruff,[2] platinum is a perfectly suitable material at temperatures of about 400°C and below.

f. <u>UF_6 and UF_4. Uranium pentafluoride,</u> UF_5 .

It was found that liquid UF_6 combines with UF_4 at about 100°C, forming a white solid of the empirical formula UF_5. The latter probably should be better formulated as a complex

$$[UF_4 \cdot UF_6]$$

since it readily decomposes into its components according to the equation

$$2UF_5 \rightarrow UF_4 + UF_6$$

The pentafluoride does <u>not</u> lose UF_6 at 100°C, even in a vacuum of 2 mm of mercury, but does begin to decompose at that pressure at about 175°C. The decomposition becomes rapid at 200° and is practically complete at 300° in accordance with the above equation; above 400°C no UF_6 remains in combination with the UF_4.

This compound is perhaps identical with the one produced by Ruff in his HF experiments (see p. 4.) although he claims that he had an addition compound with HF in his hands.

The compound can be readily prepared by placing anhydrous UF_4 in a small copper container, distilling on it an excess of UF_6, closing the valve on the copper container and heating it in a boiling water bath for about an hour, and then distilling off the uncombined UF_6 in a vacuum.

g. Behavior toward glasses.

Ordinary glass and Pyrex glass are attached by UF_6 in the presence of a small amount of water or hydrogen fluoride. This attack can be substantially averted by the use of getters as described on p. 15.

Aluminum phosphate glasses.

Recently silica free glasses, consisting mostly of aluminum phosphate have been specially prepared for our purposes. These perfectly clear glasses show high resistance against hydrated and anhydrous liquid hydrogen fluoride. It was found that these same glasses show no visible reaction with liquid UF_6 when heated for a period of a few hours to 100°C. They therefore can be conveniently used as sight glasses, etc., in apparatus for carrying out reactions with UF_6, either in the presence or absence of hydrogen fluoride.

Vycor glass.

The very porous Vycor glass, a recent product of the Corning Glass Works, showed no visible attack at room temperature when sealed with UF_6 for a period of a few weeks. Further tests are necessary, however, to determine to what extent its porosity is affected.

h. Behavior with fluorocarbons. (see p. 15).

E. Behavior of UF_6 toward Organic Compounds

This section may be conveniently subdivided as follows:

1. Hydrocarbons
2. Halogenated hydrocarbons
3. Fluorocarbons of J. Simons.

1. Hydrocarbons

1a. UF_6 and normal cetane.

Liquid normal cetane, $N-C_{16}H_{34}$, reacts rapidly with UF_6, at room temperatures, reducing the latter to UF_4. Simultaneously HF is involved and a carbonaceous deposit is formed.

1b. High vacuum oil.

The vacuum pump oil tested was of the usual quality used in the United States (from Central Scientific Co.). It was a clear, thick, yellow-orange oil and contained some unsaturated hydrocarbons since it reacted with concentrated sulfuric acid in a fashion characteristic of olefins.

In contrast to liquid paraffins it shows no violent reaction and <u>no reduction</u> of UF_6 to UF_4 takes place. However, the gaseous UF_6 does gradually disappear and forms an elastic and strong skin on the surface of the oil. Water decomposes this skin and seemingly unchanged oil is recovered. Based on this meager information one may make the tentative assumption that the unsaturated carbon linkages in the oil form some sort of an addition compound with UF_6.

1c. Butyl rubber.

Butyl rubber, a recent product manufactured by the Standard Oil Company of New Jersey, was found to show no visible reaction with UF_6 for 300 hours at 25°C.

A black variety of Butyl rubber was found to be perfectly stable toward liquid UF_6 at 100°C for six hours. This treatment did not seem to affect the elastic properties of the Butyl rubber.

2. Behavior toward Halogenated Hydrocarbons.

2a. Symmetrical tetrachloro-ethane, $HCl_2C.CCl_2H$.

In line with Otto Ruff's observation,② it was found that symmetrical tetrachloro-ethane dissolves UF_6, forming an orange yellow solution which is quite stable. At room temperature it reacts very slowly, (of the order of a few weeks) forming green UF_4. On boiling the yellow solution becomes colorless and regains its yellow color when it redissolves UF_6, indicating that the color is due to some complex between the two compounds.

2b. Pentachloro-ethane, $CCl_3.CCl_2H$.

Pentachloro-ethane also gives a yellow solution which becomes colorless on boiling. The yellow solution deposits nice crystals of UF_6 on cooling. This solvent is much stabler than the previous one, and the solution shows only small decomposition after a period of a few weeks.

2c. 1, 2,-difluoro-1,1,2,2-tetrachloro-ethane, $FCl_2C \cdot CCl_2F$.

It was thought that substitution of the hydrogen atoms of the above compound by fluorine would give a stable solvent. However, this proved not to be the case. The UF_6 reacted in a molar ratio of 1 to 1, with the compound, very probably according to the equation

$$UF_6 + C_2\ Cl_4F_2 \rightarrow UF_4\ 2C\ Cl_2F_2\uparrow$$

The reaction is pretty rapid, and is accompanied by a gas evolution. (CCl_2F_2 has a boiling point = -30° at 760 mm). After a while all of the UF_6 is converted. The reaction mixture on warming up and distilling consists of the pure original fluorochloro-carbon, and shows its original melting point of +19.5 to +20°.

2d. Trichloro-ethylene, $Cl_2C{=}CClH$.

Immediate reaction takes place and the UF_6 is reduced to UF_4.

3. Others.

UF_6 and fluoro carbons.

It was found that a mixture of fluoro-carbons, boiling in the range of +3 to 80°C and prepared by Prof. J. Simons of Pennsylvania State College, is the best solvent so far found for UF_6. This mixture of fluoro-carbons, consisting mostly of fluoropentanes and -hexanes, dissolves large quantities of UF_6, forming a perfectly colorless solution that remains unchanged for periods of months at room temperature.

It has also been heated to 100° for periods of a few hours without any apparent reaction.

The UF_6 can be very nicely crystallized from the solution.

F. Handling of UF_6 in Glass Vessels in the Presence of Getters.

UF_6 attacks glass, either Pyrex or Jena, quite rapidly, unless it is absolutely free from HF or H_2O. In the past, this writer[3] has resorted to P_2O_5 as a drying agent. This is satisfactory, but quite troublesome and time consuming.

The attack on glass is due to the following cycle of reactions:

$$UF_6 + 2H_2O \rightarrow UO_2F_2 \quad 4HF \quad \ldots\ldots \quad A$$

$$SiO_2 + 4HF \rightarrow SiF_4 \quad 2H_2O \quad \ldots\ldots \quad B$$

The water consumed in reaction A is regenerated in reaction B and therefore acts as a catalyst.

It was possible to stop this catalytic cycle by means of getters. As such powdered dry NaF and KF were found to be very efficient. These substances are known to combine with all impurities likely to occur in a glass system, i.e. with HF (forming KF, HF), H_2O (forming KF, $2H_2O$, etc.) and SiF (to K_2SiF_2). Their use may have been discouraged by the statements of O. Ruff[1,2] that UF_6 combines energetically with both KF and NaF. Fortunately this statement proved to be erroneous; we found that pure UF_6 can be kept for months over KF and NaF without any reaction. Addition does take place, however, in the presence of KF and H_2O (which of course immediately generates HF from UF_6) with the formation of <u>stable orange-yellow triple compounds</u> of the general formula

$$x\,KF,\ y\,HF,\ z\,UF_6 \text{ or } x\,NaF,\ y\,HF,\ z\,UF_6$$

The consumption of UF_6 takes place, and this is of course the crucial point, <u>only</u> in a stochiometric ratio to the amount of HF (or H_2O) present. If the latter is present in traces only a trace of UF_6 will be consumed.

For practical purposes one has only to insert into the air dry glass apparatus, some dry powered KF (or NaF). An amount corresponding to about 5% by weight of UF_6 is usually sufficient. (Since KF is quite hygroscopic it is recommended to prepare it by heating some KF, HF in a platinum dish till all HF is volatilized (red heat!), and to powder it, while still hot, in a warm mortar. Such dry KF may be stored in a P_2O_5-dessicator). The UF_6 is distilled on to the KF and mixed by shaking. When distilled over to any desired part of the apparatus it is found to be free from glass etching impurities.

Comparative tests showed that whereas without KF or NaF glass is rapidly attacked, it stays clear for months in the presence of these fluoride getters.

Literature References

1. O. Ruff and A. Heinzelmann, Berichte 42, 495 (1909).

2. O. huff and A. Heinzelmann, Zeitschrift anorganische Chemie 72, 63 (1911).

3. A. V. Grosse, Zeit, anorganische Chemie, 204, 184 (1932).

4. P. Herkel and \ . Klenau, Zeit, anorg. Chem. 222, 70 (1935)

5. H. Braune and P. Pinnow, Zeit, physik, Chem., Abt. B., 35, 239 (1937).

Appendix

Notes on Decomposition of UF_6 by Various Materials

by P. H. Abelson

The decomposition of UF_6 in the presence of a number of substances has been tested. A surprising result is the fact that at 240°C duralumin is almost as non-corroded as nickel. With the materials tested so far the following order of merit is established.

Nickel - tops
Duralumin - close second
Monel - poor third
Copper - almost tied with monel
Brass)
easy flow) far outclassed
hard solder)

Tests were performed as follows:

300 cm.^{2} of duralumin was sealed inside of a nickel container possessing 150 cm^2 surface. The container was conditioned for two hours at room temperature with fluorine gas. Forty grams of UF^6 were volatilized into the container which was then sealed. After exposure to a temperature of 240°C for 24 hours UF_6 was removed and 60 mgs. of non-volatile uranium salt were recovered. The shiny duralumin surface was tarnished but only slightly.

Test of copper and easy flow hard solder:

A copper container with an inner cylinder coated with easy flow, presenting 75 cm.^{2} of solder surface was conditioned with fluorine at room temperature for an hour.

Forty grams of UF_6 were volatilized into the container. The container was maintained at 250°C for 48 hours. At the end of that time no UF_6 was left. The major portion was found forming an adherent coating to the solder. Some coating also was found on the copper and this was smooth and adherent. The copper surface of 100 cm.^{2} had about 300 mg. of UF_4 clinging to it.

Further test on copper and brass.

A copper container was exposed to UF_6 for a week at 160°C. Parts of the 150 cm.^{2} surface showed no evidence of attack. Total adherent layer of the order of 100 mgs. Brass ends of the container were covered by a heavy adherent layer.

Test on monel.

A 48-hour exposure of UF_6 to monel resulted in rather heavy attack on this alloy. At 250°C monel appears to be about comparable to copper. It is not more than three times as good.

Further experiments employing more strenuous fluorine conditioning and more strenuous UF_6 exposure temperatures are contemplated. It is planned that other materials shall be tested.