passed through the reactor at 235°. The effluent gaseous products of the reaction were found to be as follows

	Per cent.
Propylene	61.3
n-Butane	17.3
Ethane	8.5
Ethylene	2.0
Propane	2.0
Straight chain pentenes	1.3
n-Pentane	1.1
Methane	0.9
Isopentane	0.7
Others	4.9

The liquid products collected were water-washed and fractionated. Cut I (20–54°) was water-washed to remove some acetone and analyzed by infrared absorption. Its hydrocarbon composition was 50% isopentane, 25% *n*-pentane, 10% 1-pentene and 5% each of 2-pentene, 2-methyl-1-butene and 2-methyl-2-butene. The 54–57° fraction was almost entirely acetone, and the very small amount of water-insoluble organic material (b. p. 70–71°) was not analyzed further. A small intermediate fraction (57–91°) was washed with hydroxylamine hydrochloride solution and dried; infrared analysis showed 5% of a 1-olefin, 60% 3-methylhexane and 30% 2-methylhexane. The remaining 5% was ketone which was not completely removed by water-washing. Cut IV (b. p. 91–94) was washed with concentrated sulfuric acid with virtually no change in volume or the refractive index of 1.3890. Infrared analysis identified the material as 3-methylhexane and a vapor density measurement gave the molecular weight as 100 (theory 100.2). The decane fraction (153–161°) after being washed with concentrated sulfuric acid and 6 *N* sodium hydroxide analyzed as follows: carbon 84.4%, hydrogen 15.4%, mol. wt. 149; calcd., 84.5, 15.5 and 142, respectively.

TABLE VII

YIELD OF HIGHER HYDROCARBONS DERIVED FROM PROPYLENE (BASED ON DI-*t*-AMYL PEROXIDE)

Product	Per cent.
Amylenes	2.7
n-Pentane	2.5
Isopentane	1.6
3-Methylhexane	8.0
Nonenes and decanes	3.0

Acknowledgment.—The authors are indebted to the members of the Spectroscopic Department of This Company, and in particular to Dr. R. S. Rasmussen, for the infrared analyses.

Summary

1. The di-*t*-alkyl peroxides are especially useful tools for the study of free radical processes.

2. Some of the products from the interaction of free methyl and ethyl with various saturated and unsaturated hydrocarbons have been isolated and identified. Mechanisms of formation of these compounds are suggested.

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[7] Original manuscript received September 26, 1946.

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY OF THE IOWA STATE COLLEGE]

The Structures of the Carbides, Nitrides and Oxides of Uranium[1]

BY R. E. RUNDLE, N. C. BAENZIGER, A. S. WILSON AND R. A. MCDONALD

Introduction

The systems uranium–carbon, uranium–nitrogen and uranium–oxygen have been given thorough X-ray study in the course of work carried out for the Metallurgical Project. In this paper this work will be summarized rather briefly, giving pertinent structural information and necessary details concerning the methods used in carrying out the work.

In general, little discussion of the structures will be presented here. The nature of the metal-like monocarbide, mononitride and monoxide are discussed elsewhere along with other similar compounds.[2] Since the structures of nearly all the phases examined have been simple, parameterless structures of types described thoroughly in "Strukturbericht," it has seemed unnecessary to present lengthy accounts of the structural determinations, together with tables of calculated and observed intensities. In every case not otherwise indicated a careful comparison of observed and calculated intensities for the assigned structure has been made.

Though this paper is intended primarily as a summary of X-ray structures, many of the compounds whose structures are reported here were discovered and their compositions first obtained either solely by X-ray study or jointly with chemical investigations. It seems well to point out, therefore, that X-ray study of the carbides, nitrides and oxides of uranium has required extensive revision of formulas in these systems. The monocarbide and the mononitride were discovered, with chemical and metallographic aid, by X-ray diffraction; the monoxide was found solely by X-ray diffraction. Not a single nitride of uranium had been assigned a correct formula before these X-ray studies were made.[3] Even among the higher oxides new phases were found, and the relationships among the higher oxides

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[1] Paper No. 7 of the Institute for Atomic Research. Work done under contract W-7405 eng-92, Manhattan Project, U. S. Corps of Engineers. F. H. Spedding, Project Director. A review of this work will be published in Div. VIII, Manhattan Project Technical Series.

[2] R. Rundle, "A New Interpretation of Interstitial Compounds," submitted for publication in *Acta Crystallographica*.

[3] Gmelin's "Handbuch der anorganischen Chemie," system Number 55, Verlag Chemie, Berlin, 1936, p. 107 ff.

and nitrides turned out to be more complex than hitherto suspected.

Most of the compounds reported here are prepared by the reaction of solids to form solid products which are difficult to handle chemically. The fact that X-ray study has required extensive revision of formulas in the systems provides an example of the serious errors which can arise in the interpretation of solid–solid reactions by purely chemical examination.

The authors do not wish to imply that unaided X-ray study is a substitute for unaided chemical study. The authors have had the full coöperation of metallographic, inorganic and analytical chemists in preparing and determining the compositions of the compounds reported here. Indeed, much of this work originated with metallographic or inorganic studies of uranium systems.

It must be pointed out that determination of compositions of phases involving light elements and uranium is generally possible only in the case of relatively simple structures. It is, of course, nearly impossible to locate light elements in the presence of uranium, particularly in structures involving parameters. Consequently, even in those cases where X-ray study gave a clear indication of composition, confirmation by analytical chemists was sought.

Uranium Carbides

Uranium Monocarbide.[4]—The lowest carbide of uranium is the monocarbide, UC. Dendritic material of this composition can be separated even from uranium metal of very low carbon content by dissolving the metal preferentially with dilute acids. X-Ray diagrams of dendritic material were identical with diagrams of material prepared from metal and carbon at the stoichiometric ratio, UC. Other methods of preparation are described below.

Uranium monocarbide is face-centered cubic, $a = 4.951 \pm 0.001$ Å., with four "molecules" per unit cell. The X-ray density is, then, 13.63 g./cc.

The possible structures are the sodium chloride- and zinc-blende-types, which differ only in the positions of the carbon atoms. Although relative to uranium the X-ray scattering power of carbon is very slight, it appears possible to differentiate between these two structures by examining the pair of reflections (331) and (420). These reflections have the same multiplicity factor and are separated by only three degrees on X-ray diagrams made with CuKα radiation. The intensity factors dependent upon scattering angle only may, therefore, be considered essentially identical, particularly in the neighborhood $2\theta = 90°$, where these reflections occur.

For the sodium chloride-type structure the structure factors for (331) and (420) are $(4f_u - 4f_c)$ and $(4f_u + 4f_c)$, respectively, where f represents the atom form factor. For the zinkblende-type structure the corresponding structure factors are $(4f_u - 4if_c)$ and $(4f_u - 4f_c)$. For the sodium chloride-type structure $I_{(420)} > I_{(331)}$ by about 14%, while for the zinkblende-type structure, $I_{(331)} > I_{(420)}$ by about 7%. (The values of the atom form factor used in these calculations, $f_u = 54.3$, $f_c = 1.8$, are those for uranium and carbon atoms. Actually this is the most unfavorable case, since there may be some transfer of electrons from the electropositive to the electronegative element. Similar intensity comparisons have been made for uranium mononitride and monoxide, where the intensity ratios are greater, due to larger scattering of nitrogen and oxygen.) On X-ray powder diagrams made using cylindrical, well-powdered samples (420) was clearly more intense than (331). Other intensity comparisons, while not as critical as the above, also support the sodium chloride-type structure.

Range of Composition of the Monocarbide Phase.—Precise values of the lattice constant of the monocarbide have been obtained for samples containing excess carbon and for others containing excess metal. In a large group of samples of various compositions, lattice constants ranging from 4.947 to 4.951 Å. have been observed, but these varied at random and were in no way related to composition. Dendritic samples, which probably contain all the oxygen and nitrogen impurities of the metal, have spacings of about 4.948 Å. The isomorphous monoxide and mononitride of uranium are known to have smaller lattice constants than the carbide (see below). We presume, therefore, that the composition of the monocarbide is quite definite in the absence of nitrogen and oxygen, and that the largest spacing observed, 4.951 Å., represents the best value of the lattice constant of the monocarbide. The solubility of both carbon and uranium in the monocarbide is negligible at room temperature.

Solubility of Nitrogen and Oxygen in the Monocarbide.—A striking example of the interchange of nitrogen atoms for carbon atoms in the uranium monocarbide lattice is shown by by the following experiment. Mr. P. Chiotti of this Laboratory has heated uranium monocarbide and uranium mononitride at 1950° for fifteen minutes. Precision X-ray diagrams of the sample showed that the spacing of the uranium monocarbide had changed from $a = 4.947$ to 4.921 Å., and that of uranium mononitride from 4.883 to 4.917 Å. After longer heating the sample would undoubtedly come to equilibrium with just one spacing of approximately 4.92 Å.

Similar experiments with the isomorphous uranium monoxide are more difficult to carry out since uranium monoxide cannot be prepared in pure form. However, in systems in which oxygen was the principle contaminant, the monocarbide spacing was considerably lowered.

In the case of mononitride and monocarbide, complete solid miscibility has been demonstrated.

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(4) Mostly from Metallurgical Project Report CT-686, May (1943).

It appears likely that monoxide and monocarbide are also completely miscible. In view of the very similar lattice spacings of carbide (4.951), oxide (4.91) and nitride (4.880) this is not surprising.

Uranium Sesquicarbide.[5]—U_2C_3 is the next phase of higher carbon content. This phase, which exists only at very high temperatures, has resisted all attempts to quench it to room temperature. Samples of the composition U_2C_3 quenched from well above 2000° are two-phase, uranium monocarbide and uranium dicarbide, as shown by powder diagrams and by microscopic examination. The microscopic and X-ray investigations do indicate, however, that at very high temperatures (probably above 2000°) uranium sesquicarbide must indeed exist. At the composition U_2C_3 what appear superficially to be single crystals are formed in the melt. At room temperature these "single crystals" give broad but definite, single-crystal X-ray reflections, but the reflections are due to both uranium monocarbide and dicarbide arranged so that their crystal axes are mutually parallel to the main edges of the apparently single crystal. Microscopic examination reveals a Widmanstatten structure. Quite apparently the sesquicarbide forms at high temperatures but decomposes to the mono- and dicarbides at lower temperatures.

Uranium Dicarbide.—Uranium dicarbide is the only carbide whose X-ray structure had been reported previously in the literature.[6] Its structure then was established as isomorphous with calcium dicarbide. Since purer uranium was available to this laboratory than to earlier workers, the lattice constants of the dicarbide were re-examined.

The lattice constants of the body-centered, tetragonal dicarbide vary with the previous heat treatment of the sample; all samples which were cooled slowly to room temperature had lattice constants independent of carbon content, $a = 3.517 \pm 0.001$ Å., $c = 5.987 \pm 0.001$ Å. Samples which contained an excess of carbon (about 10–11 weight per cent. carbon) and which were quenched from 2400 and 2700° had much smaller lattice constants: $a = 3.504 \pm 0.001$ Å., $c = 5.951 \pm 0.001$ Å. and $a = 3.507 \pm 0.001$ Å., $c = 5.962 \pm 0.001$ Å. for samples quenched from the two temperatures. X-Ray diagrams of the samples allowed to cool slowly to room temperature contained maxima of the monocarbide and carbon as well as that of uranium dicarbide. The lattice constants of the dicarbide had increased to that for slowly cooled samples.

Apparently carbon dissolves in the dicarbide at higher temperatures and may be maintained in solution by quenching. Samples which are not quenched not only precipitate carbon, but also apparently yield monocarbide and more carbon through decomposition of the dicarbide at some intermediate temperature. Unlike the sesquicarbide, however, the dicarbide is easily quenched.

The decrease in lattice constants with increased carbon solubility may be explained in several ways. Either an uranium atom is occasionally replaced by a carbon atom or C_2 group, or the structure containing excess carbon must be thought of as a uranium dicarbide lattice deficient in uranium, allowing cell dimensions to shrink slightly.

Previously the carbon positions in uranium dicarbide had been assumed to be like those in calcium carbide. Because of the different chemical properties of calcium and uranium dicarbides, it does not appear that the uranium dicarbide can be regarded as a salt of acetylene. Accordingly, we have tried to see if anything can be said about the carbon positions from intensity considerations.

Reflections differing only in carbon contributions and close enough together to be compared with reliability are rare for powder diagrams of uranium dicarbide. However, reflections (204) and (310) meet these requirements. M. von Stackelberg has discussed the possible structures,[7] and we have considered these for uranium dicarbide.

With U at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ there are five possible sets of body-centered positions for the carbon atoms. These are

A $000, \frac{1}{2}\frac{1}{2}\frac{1}{2} + 00z, 00\bar{z}$
B $000, \frac{1}{2}\frac{1}{2}\frac{1}{2} + 0\frac{1}{2}z, \frac{1}{2}0\bar{z}$
C $000, \frac{1}{2}\frac{1}{2}\frac{1}{2} + 0\frac{1}{2}0, \frac{1}{2}00$
D $000, \frac{1}{2}\frac{1}{2}\frac{1}{2} + 0\frac{1}{2}\frac{1}{4}, \frac{1}{2}0\frac{1}{4}$
E $000, \frac{1}{2}\frac{1}{2}\frac{1}{2} + 0\frac{1}{2}z, \frac{1}{2}0z$

Structures A and B permit C_2 groups. A is the calcium carbide structure, and B is related to the zinkblende structure, with C_2 groups parallel to the *c* axis replacing a monatomic ion.

If C_2 groups with a C–C distance equal to that in acetylene are assumed, then z in structures A and B becomes approximately 0.4 and 0.15, respectively. One then finds that for structure A, $I_{(204)}/I_{(310)} = 26/34$, while for B, $I_{(204)}/I_{(310)} = 26/26$. (Atom form factors were chosen in the same manner as for the monocarbide.) On powder diagrams (310) is clearly more intense than (204), so that if there are C_2 groups, the calcium carbide-type structure must be chosen.

Structures C and D make $I_{(204)} > I_{(310)}$ and can be eliminated Structure E with $z = 1/8$ or $3/8$ is satisfactory as far as the intensity comparisons are concerned, but it does not seem to be a reasonable structure, in that there are four carbon atoms bonded very closely to uranium at about 1.90 Å. This bond is shorter than the sum of the covalent radii of uranium and carbon (2.17 Å.). Moreover, all four carbons would lie on one side of uranium, with no good bonds on the other side. We consider that these intensity considerations, while fragmentary, support C_2 groups and the calcium carbide-type structure for uranium dicarbide.

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(5) Largely from Metallurgical Project Report CT-751A, June (1943).

(6) G. Hägg, *ibid.*, **B12**, 12 (1931).

(7) M. v. Stackelberg, *ibid.*, **B9**, 437 (1930).

Uranium Nitrides

Uranium Mononitride.[8]—Uranium mononitride, UN, is the lowest nitride of uranium. Its face-centered cubic lattice constant is $a = 4.880$ Å.; its X-ray density, $\rho = 14.32$ g./cc. It is entirely isomorphous with uranium monocarbide. Here again a comparison of the intensities of reflections (420) and (331) shows (420) as the stronger reflection, indicating the sodium chloride-type structure.

Uranium mononitride heated with uranium to high temperatures does not change its lattice constant beyond the limit of error. If the mononitride is treated with more nitrogen, a second phase with the composition U_2N_3 appears, but the lattice constant of the mononitride remains unchanged. Thus, the solubility of either nitrogen or uranium in the mononitride is vanishingly small.

Uranium Sesquinitride.[8]—Uranium sesquinitride, U_2N_3, is body-centered cubic, $a = 10.678 \pm 0.005$ Å., $Z = 16$, $\rho = 11.24$ g./cc. The structure of this phase is isomorphous with manganese sesquioxide (Type $D5_3$ in the "Strukturbericht" designation). The location of the uranium atoms requires one parameter, which has been found to be -0.018 at the ideal composition.[9] Nitrogen positions presumably are similar to those of oxygen in manganese sesquioxide. Since the structure is a well known type, the structure determination will not be reproduced here, nor will atomic positions be listed.

The lattice constant of uranium sesquinitride has been studied as a function of composition by heating uranium sesquinitride with uranium mononitride and uranium. Detectable changes in the constant cannot be produced on the low nitrogen side of the composition U_2N_3, so the phase must not exist below this ideal composition.

Uranium Dinitride and the Phase Between the Sesquinitride and Dinitride.[8]—The sesquinitride structure is very similar to the fluorite-type structure. Indeed, if the weak reflections from uranium sesquinitride were ignored a face-centered cubic pseudo-lattice, $a = 5.339$ Å. (half the true lattice constant), could be chosen. This is nearly identical with that of the dinitride which has the fluorite structure.

The sesquinitride structure is essentially a distorted fluorite-type structure with nitrogen missing in a regular way from the lattice.[10] As nitrogen is added to the sesquinitride the distortion in the structure from that of the fluorite-type decreases and the system remains one phase. This is shown by the gradual decrease in intensity of the weak lines of the uranium sesquinitride structure, corresponding to a change of the uranium parameter from -0.018 toward zero.

At a nitrogen pressure of one atmosphere the maximum obtainable nitrogen–uranium ratio seems to be about 1.75, which probably accounts for the fact that U_4N_7 and other unusual formulas for uranium nitrides have been reported in the literature. Compositions in this range at ordinary pressures are determined by the pressure and temperature of preparation of the nitride, and, since the system remains one phase throughout the region from uranium sesquinitride to dinitride, only the extreme ends of the phase need be considered as distinct compounds.

In the one-phase region between uranium sesquinitride and dinitride the lattice constant decreases with increasing nitrogen content, at least up to the composition $UN_{1.75}$. At $UN_{1.5}$, $a = 10.678 \pm 0.005$ Å., while at $UN_{1.75}$, $a = 10.580 \pm 0.005$ Å. At $UN_{1.75}$ the maxima requiring the doubled unit are just barely visible. Presumably this decrease in lattice constant is due to a shift toward a more closely packed structure as the distortion, occasioned by nitrogen missing from the fluorite-type structure, is removed.

Samples prepared at high nitrogen pressures (126 atm. nitrogen) in the composition range UN to UN_2 are two-phase, consisting of UN and UN_2. Here the UN_2 phase has the ideal fluorite structure and a lattice constant, $a = 5.31 \pm 0.01$ Å. Apparently at high pressures U_2N_3 disproportionates into the mono- and dinitrides. This is to be expected from the change in volume in the reaction

$$U_2N_3 = UN + UN_2$$

The unit volume of U_2N_3 is 1217.5 Å.^{3} and the corresponding volume for UN plus UN_2 is 1057 Å.^{3} The volume decrease is thus about 13%.

It is to be noted, however, that between $UN_{1.75}$ and UN_2 the lattice expands, since at $UN_{1.75}$ the lattice constant is 10.58 ± 0.01 Å. and twice the lattice constant of UN_2 is 10.62 ± 0.02 Å. Pure UN_2 seems to be difficult to prepare, as most samples of nitrides prepared at high pressures contained some UN, but in a few cases the UN_2 phase was pure, at least to the extent that UN reflections could no longer be detected on X-ray diagrams.

Uranium Oxides

Uranium Monoxide.[11]—Uranium monoxide is face-centered cubic, $a = 4.92 \pm 0.02$ Å. with the sodium chloride-type structure. (The evidence for the sodium chloride structure is again the comparison of reflections (331) and (420).) Since uranium monoxide has never been prepared in any quantity and is known only from X-ray data, it seems necessary to describe its preparation and the nature of the evidence for the compound.

The monoxide was discovered during attempts to make X-ray diagrams of uranium metal in the beta and gamma temperature ranges. The diagrams, in almost all cases, consisted chiefly of a

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(8) From Metallurgical Project Reports CT-686, May (1943) and CC-1524, March (1944).

(9) Parameter as listed in "Strukturbericht," Vol. II, 38 (1937).

(10) For a more complete description of the relation between these structures see "Strukturbericht," ref. 9.

(11) Metallurgical Project Reports CN-1495, April (1944), and CC-1984, Dec. (1944). British workers found this oxide independently at a later date.

face-centered cubic phase, $a = 49.1$ Å. The metal had been previously cleaned, and was contained in carefully evacuated, quartz capillaries which had been cleaned up with a zirconium getter. The metal was kept away from the quartz with columbium metal spacers. The chief contaminant in these samples was known to be oxygen.

Later it was found that a uranium metal surface which has become badly discolored due to "oxidation" continues to give a powder diagram characteristic of the metal until heated. The gold or even black coating disappears on heating, producing a metallic-looking surface somewhat whiter in appearance than uranium itself. The surface after heating produces an X-ray diagram of a face-centered cubic phase, $a = 4.91$ Å. The chief impurity in the surface is oxygen, though small amounts of nitrogen and carbon also are present.

Attempts to prepare the monoxide by heating UO_2 or a higher oxide with metal have usually been disappointing. Generally the high temperature necessary has caused considerable contamination by carbon (from graphite heating elements in some cases). Where carbon and nitrogen have been very carefully excluded little or no reaction has resulted. In cases of considerable carbon contamination the face-centered phase was produced. In these instances oxygen was the chief light element of the UX phase. Though it seems probable that carbon is necessary only to promote the reaction of a higher oxide with uranium to form UO, the possibility cannot be excluded that some UC or UN must be present for the phase to form. It may be possible that UO should be described as a UX phase, where X is carbon, nitrogen and oxygen, but that the amount of oxygen in the phase can be made to predominate.

Due to the fact that UO has never been prepared with great purity, the spacing is not known precisely. The spacing lies between that of the carbide and the nitride. Spacings between 4.93 and 4.91 Å. have been observed. Since carbon contamination has generally exceeded nitrogen contamination, the lower spacing is probably more nearly correct.

Uranium Dioxide.—Uranium dioxide has been investigated by many early workers in the field of X-ray diffraction.[12] Various values of the cubic spacing have been reported, so it was thought well to check the values with a sample of the very pure oxide available on this project. The lattice constant of such a sample is $a = 5.4581 \pm 0.0005$ Å.

Subsequent investigation showed that a wide variation in spacing is possible due to solubility in uranium dioxide. When the oxide is heated with uranium above 2000°, as in making the monoxide, the dioxide spacing is increased to $a = 5.4610 \pm 0.0007$ Å. Presumably in this region uranium is introduced into the vacant set of cubic interstices in the uranium dioxide structure. As one increases the oxygen content by heating uranium dioxide with U_3O_8 in a sealed quartz system, the lattice constant of the dioxide decreases in magnitude, finally reaching $a = 5.4297 \pm 0.0008$ Å. as a limit. A new phase appears in a sample of composition $UO_{2.3}$, so the limit of the solubility region must lie between $UO_{2.2}$ and $UO_{2.3}$.

Uranium dioxide has the fluorite structure. This may be considered as a simple cubic lattice of oxygen ions with U^{+4} ions in one half of the cubic interstices. If the oxygen ion lattice remains fixed but U^{+4} ions are occasionally missing at random from the lattice, the oxygen lattice would be allowed to shrink slightly giving the lower lattice constants. If the density is calculated on this assumption, using $UO_{2.25}$ as the limiting composition, the density would change from 10.96 g./cc. for pure uranium dioxide to 10.04 g./cc. for $UO_{2.25}$.

Biltz and Müller have examined the uranium–oxygen system and have found a discontinuity in both vapor pressure and molecular volume at $UO_{2.25}$ in agreement with the X-ray data.[13] They have reported an increase in densities with composition in this region for samples prepared above 1000° and a decrease in density for samples prepared below 1000°. The reliability of these observations is open to question since by a different choice of their densities, the opposite trend may be shown. Moreover, their experimental value for the density of UO_2 is 10.73 to 10.82 g./cc., well below the calculated X-ray density, and the highest density reported in the whole region above uranium dioxide (with one exception) is less than the calculated X-ray density of uranium dioxide. Since densities measured by liquid displacement methods are subject to errors due to micro cracks and fissures, the data of Biltz and Müller cannot finally decide the type of solubility.

It is difficult to reconcile the decrease in lattice constant with the type of solubility requiring the introduction of additional oxygen ions into an already close-packed arrangement of oxygen ions. Accordingly, we feel that the solubility is due to the absence of U^{+4} ions rather than the presence of interstitial oxygen ions. Calculating the density on the alternative assumption that oxygen ions are being introduced into interstices in the UO_2 structure, the density would increase to 11.30 g./cc.

Higher Uranium Oxides.[14]—The oxides U_2O_5, U_3O_8, several forms of UO_3 and a hydrate of UO_4 are known. W. H. Zachariasen first examined the structures of U_3O_8, UO_3 and the hydrated UO_4. These will, presumably, be reported by him.

Biltz and Müller found that a one phase area extended from UO_3 to $UO_{2.62}$. X-Ray diagrams

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(12) V. Goldschmit and L. Thomassen, *Videnskaps Selskapets Skrifter, I. Mat.-Naturw. Klasse Kristiania*, 2 (1923); A. van Arkel, *Physica*, **4**, 286 (1924); A. Schoep and V. Billiet, *Bull. soc. geol. Belg.*, **58**, 198 (1935).

(13) W. Biltz and H. Müller, *Z. anorg. Chem.*, **163**, 257 (1927).

(14) Largely from Metallurgical Project Report CC-1980, Nov (1944).

of the samples in this range show that this one phase area is based on the "ideal" UO_3 phase. U_3O_8 has been shown to be very similar to UO_3 by W. H. Zachariasen; this has been confirmed by our data. Our X-ray evidence also indicates that this one phase area may extend to the composition $UO_{2.5}$.

X-Ray diagrams of an equimolar mixture of U_3O_8 and UO_2 were made both before and after heating to 1100°. Before heating the sample the uranium dioxide maxima were the strongest maxima in the diagram due to the higher symmetry of the phase. After heating the sample the $UO_{2.25}$ maxima, although present, were weak and the U_3O_8 maxima had shifted in position and intensity. By examination of known mixtures of U_3O_8 and UO_2 it was possible to estimate the relative amounts of the phases present in the $UO_{2.5}$ sample. The upper bound on the lower limit of the composition of the UO_3-like phase was found to be $UO_{2.52}$.

By chance single crystals of $UO_{2.5}$ have been obtained by thermal decomposition of UO_2Cl_2. Powder diagrams of these needles were identical with those of $UO_{2.5}$ as described above. A detailed structure of U_2O_5 will be given later. However, the unit cell can be reported as orthorhombic, $a = 8.27 \pm 0.02$ Å., $b = 31.65 \pm 0.1$ Å., $c = 6.72 \pm 0.02$ Å., with 16 U_2O_5 per unit cell. There is a pseudo cell with $a = 4.135$ Å., $b = 3.956$ Å., $c = 6.72$ Å. The X-ray density is 8.35 g./cc.

Experimental

Methods.—X-Ray diagrams were made using Debye-Scherrer powder cameras of 5.73 and 5 cm. radius with the exception of the oxide samples in the composition range uranium dioxide to trioxide. These diagrams were obtained using an unsymmetrical self-focusing powder camera of 10 cm. radius manufactured by the Wyland Company. This camera gave very high dispersion and was ideally suited for the examination of the complex phases between uranium dioxide and trioxide. Nickel filtered CuK radiation was used in all but precision diagrams. Precision diagrams were prepared using a symmetrical self-focusing, back-reflection camera manufactured by the Wyland Co. Unfiltered CuK radiation and the mixed radiations of a copper-nickel alloy target were used to obtain more lines in the back reflection region. The data were evaluated using Cohen's method. The limit of error, when reported, is the standard error as determined from the measurement of one film.

X-Ray densities were calculated according to the suggestion of Jette and Foote using the formula $\rho = 1.65023\ MN/V$, where M is the molecular weight, N is the number of molecules per unit cell, and V is the volume of the unit cell calculated in terms of Siegbahn wave lengths.[15]

Preparation of Samples.—Most of the samples were prepared by other members of the Ames laboratory of the Manhattan Project. The general methods of preparation are given below.

Uranium Carbides.—Messrs. A. Daane, A. Snow, P. Chiotti and H. Carter prepared the carbide samples. The carbides were prepared by the direct reaction of appropriate amounts of uranium or uranium oxide and carbon in graphite crucibles at elevated temperatures obtained by induction heating. Samples were subsequently analyzed for carbon, since some carbon was dissolved from the crucibles. A. Tevebaugh separated uranium monocarbide dendrites from uranium by using dilute hydrochloric acid containing some hydrogen peroxide.

Metallographic study of the uranium carbon system by the above members of the Ames metallographic group is reported elsewhere. The metallographic reports contain additional information on the uranium-carbon system.[16]

Uranium Nitrides.—A. Newton prepared most of the nitride samples except those at high pressure. A. Daane first prepared uranium mononitride by the thermal decomposition of higher nitrides of uranium in a vacuum. It may also be prepared by heating uranium and the higher nitrides at elevated temperatures, the reduction of higher nitrides with hydrogen, the direct reaction of ammonia or nitrogen with uranium hydride and the direct reaction of nitrogen and uranium. Higher nitrides were prepared by the direct reaction of either nitrogen or ammonia with the hydride or the metal and by the reduction of still higher nitrides with hydrogen. The dinitride was prepared only at high pressures (about 126 atm.) of nitrogen on uranium metal. W. Tucker and P. Figard prepared the high pressure samples.

Chemical investigation of the uranium-nitrogen system has been reported by the above members of the Ames inorganic group.[17]

Uranium Oxides.—P. Chiotti, R. Raeuchle and J. Warf prepared the uranium-oxygen samples in the composition ranges between uranium and uranium dioxide by heating to over 2000° powdered metal and oxide which had been pressed into a billet. Samples of higher oxygen content than the dioxide were prepared by heating to about 1100° calculated amounts of UO_2 plus U_3O_8 or U_3O_8 plus UO_3 in sealed evacuated quartz capillaries. R. Raeuchle prepared the first U_2O_5. O. Johnson prepared single crystals of U_2O_5 by thermal decomposition of UO_2Cl_2 at 900°. The UO_2, U_3O_8, and UO_3 used were the pure materials available on the Manhattan Project.

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Summary

1. Uranium monocarbide is face-centered cubic, $a = 4.951$ Å., and has the sodium chloride-type structure. Uranium dicarbide is body-centered tetragonal, $a = 3.517$ Å., $c = 5.987$ Å., and has the calcium carbide structure. Carbon is soluble in the dicarbide at high temperatures, and the dicarbide decomposes into the monocarbide and carbon at intermediate temperatures. Uranium sesquicarbide probably exists at temperatures above 2000°. It does not exist at room temperature.
2. Uranium mononitride is face-centered cubic, $a = 4.880$ Å., and has the sodium chloride-type structure. Uranium sesquinitride is body-centered cubic, $a = 10.678$ Å., and has the manganese sesquioxide structure. The uranium sesquinitride structure gradually changes toward the ideal dinitride structure in a one phase region extending to the composition $UN_{1.75}$. High pressure is needed to form the dinitride which is face-centered cubic, $a = 5.31$ Å., and has the fluorite structure.
3. Uranium monoxide is face-centered cubic, $a = 4.92$ Å., and has the sodium chloride-type

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[15] Jette and F. Foote, *Phys. Rev.*, **58**, 81 (1940).

[16] The uranium-carbon system will be reviewed in Div. VIII and Div. IV of the Manhattan Project Technical Series.

[17] Work to be reviewed in Div. VIII of the Manhattan Project Technical Series.

structure. It is very difficult to prepare free from carbon or nitrogen. Uranium dioxide has the fluorite structure, a = 5.4581 Å. Oxygen is soluble in the fluorite structure up to approximately the composition $UO_{2.25}$ at which point the lattice constant is a = 5.4297 Å. U_2O_5 is orthorhombic, a = 8.27 Å., b = 31.65 Å., c = 6.72 Å. The structure is related to those of U_3O_8 and UO_3. A one phase region exists from U_2O_5 to UO_3 in which the various structures continuously transform from one to another.

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Basic Fluorides of Aluminum

BY J. M. COWLEY AND T. R. SCOTT

Introduction

The readiness with which aluminum and fluorine form complex ions in solution has been demonstrated by Brosset,[1] who determined the proportions of ions of the type AlF_n (where n = 1 to 6) in dilute solutions at constant activity. In solutions containing both aluminum fluoride and sulfate, the complex cations AlF^{2+} and $AlF_2{}^+$ appear to predominate, and the former may well be present in the salt $AlF_3 \cdot Al_2(SO_4)_3$ or $(AlF)SO_4$, discovered by Ehret and Frere.[2] Various Russian workers, *e.g.*, Nikolaev,[3] have described the preparation of aluminum fluosulfate, $(AlF_2)_2SO_4$ or $4AlF_3 \cdot Al_2(SO_4)_3$, although Ehret and Frere found no evidence for the formation of this compound in the system AlF_3–$Al_2(SO_4)_3$–H_2O at 25°. It is thus conceivable that aluminum might form hydroxy- (or oxy-) fluorides having the compositions $AlF(OH)_2$ and $AlF_2(OH)$: methods for the preparation of the latter compound (or the oxyfluoride $(AlF_2)_2O$) have indeed been given in several Russian patents.[4,5] Apart from the work of Schober and Thilo,[6] who described the diffraction pattern of $Al_7O_{10}F$ (prepared by the thermal hydrolysis of aluminum fluoride), no X-ray diffraction studies of these compounds have been made. The present paper describes the preparation of basic fluorides with compositions varying within the limits AlF_3 and $Al(OH)_3$, and gives details of their crystallographic structures.

Experimental

The basic fluorides may be precipitated from solutions of aluminum fluosulfate by treatment with ammonia[3] or by hydrolysis at temperatures ranging from 100–180°.[4] Aluminum fluonitrate solution may also be neutralized with calcium carbonate, leaving calcium nitrate in solution and precipitating basic aluminum fluoride.[5] Solutions of aluminum fluoride undergo slight hydrolysis on boiling, but the precipitate is very gelatinous and difficult to manipulate. While it is probable that hydrolysis at 150–200° would produce basic fluorides in better yield and in more satisfactory physical form, suitable corrosion-resistant equipment for this method was not available.

For the present study, samples were prepared by the addition of ammonia to solutions of aluminum sulfate containing varied proportions of aluminum fluoride. The aluminum sulfate was of A.R. grade, while solutions of aluminum fluoride were prepared by dissolving Laboratory Reagent grade aluminum metal in A.R. hydrofluoric acid. The general reaction was

$$6NH_4OH + Al_2(SO_4)_3 + xAlF_3 \longrightarrow 3(NH_4)_2SO_4 + Al_{2+x}(OH)_6F_{3x}$$

where x was varied from 0.4 to 14.0. Nikolaev[3] used this method for the production of AlF_2OH and his directions for the use of 20% more than the theoretical quantity of ammonia and for subsequent boiling of the gelatinous suspension of basic fluoride were carefully followed. (With a greater excess of ammonia, the fluorine content of the basic fluoride is considerably reduced.) After boiling for two hours, the suspensions were filtered and the basic fluorides thoroughly washed with water. The products were dried at 130°, again washed with water to remove entrained ammonium sulfate, and dried for a further four to six hours at 130°. No sulfate could be detected in the final products, though in all instances combined ammonia was present. Attempts to prepare uncontaminated basic fluorides by other methods were no more successful. The compound obtained by hydrolysis of aluminum fluosulfate solution at 100° contained 5% of sulfate, and it is highly probable that the treatment of aluminum fluonitrate with calcium carbonate would also yield an impure product. A further sample was obtained by adding ammonia to molar aluminum fluoride solution until the pH reached 6.4, and consisted of a mixture of almost equal parts by weight of aluminum basic fluoride and ammonium tetrafluoaluminate.

All specimens were analyzed for aluminum, fluorine, silica and ammonia, the oxygen content being calculated from the atomic ratio Al:F and the water content being obtained by difference. Aluminum was precipitated and weighed as the hydroxyquinolate, after fusion of the sample with potassium pyrosulfate or digestion with concentrated sulfuric acid. Fluorine was determined by the Willard–Winter distillation followed by titration of an aliquot of the distillate with thorium nitrate solution. Silica was estimated by a distillation method[7] devised by one of the authors.

X-Ray diffraction patterns were obtained from all samples with the 14.3 cm. powder-camera of the General Electric XRD unit, using filtered cobalt Kα radiation. The powder was packed into a wedge using a dilute solution of collodion in amyl acetate as binder and rocked through an angle of 20° during the exposure. To obtain the relative intensities of the lines, a key pattern, that from sample 4 (Table II), was microphotometered and used as an intensity standard. In the powder-wedge method, the reflections at small angles are weakened by absorption. The extent of this effect was estimated by comparison of the intensities of the key pattern with those given by a fine cylindrical sample, and the appropriate correction was made to the observed intensities of the diffraction lines.

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(1) Brosset, "Electro-chemical and X-Ray Crystallographic Investigation of Complex Aluminum Fluorides," Stockholm, 1942.

(2) Ehret and Frere, THIS JOURNAL, **67**, 64 (1945).

(3) Nikolaev, *J. Chem. Ind. U. S. S. R.*, **14**, 1087 (1937).

(4) Kashcheev and Lazarev, Russian Patent 46,256 (Mar. 31, 1936).

(5) Morozov and Ivanov, Russian Patent 53,812 (Sept. 30, 1938).

(6) Schober and Thilo, *Ber.*, **73B**, 1219 (1940).

(7) Scott, *J. Council Sci. Ind. Research* (Australia), **19**, 103 (1946).