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An Annotated Bibliography of Selected References on the Solid-State Reactions of the Uranium Oxides

UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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An Annotated Bibliography of Selected References on the Solid-State Reactions of the Uranium Oxides

by S. M. Lang

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Foreword

The available information on the reactions of the uranium oxides, singly and in combination with other oxides at the high temperatures, and in the various atmospheres, encountered and anticipated in the energy-producing areas of atomic reactors, is limited.

At the request of the U. S. Atomic Energy Commission, this Circular is issued to supply the demand of numerous research groups and subcontractors of the AEC for an annotated bibliography. This bibliography on the solid-state reactions of the uranium oxides is selective in subject matter and comprehensive in content.

This Circular is not intended to supplant other annotated bibliographies of a more extensive nature. Its purpose is to centralize the information within the specific field of solid-state reactions and to record the available information since the time of earlier publications.

A. V. ASTIN, *Director*.

Contents

An Annotated Bibliography of Selected References on the Solid-State Reactions of the Uranium Oxides

By S. M. Lang

An annotated bibliography of 257 references, and about 60 not abstracted, on the solid-state reactions of the uranium oxides with 36 other oxides and on the properties, crystal structure, and solid-state reactions (including oxidation and reduction) of UO_2, U_2O_5, U_3O_8, and UO_3 as reported in the literature. Subject and author indexes are included.

Introduction

The possible use of ceramics, especially the high melting-point metallic oxides, as structural and fuel elements for atomic power reactors[1] [2] has been retarded mostly by the limited fundamental information available on the phase relations of the systems involved and on the ceramic materials themselves.

Under the sponsorship of the U. S. Atomic Energy Commission, the Porcelain and Pottery Section of the National Bureau of Standards has been studying the phase equilibria of various high-temperature systems in which one of the components is uranium dioxide (UO_2). An annotated bibliography of the reactions of the dioxide and of the oxidation and reduction of the various reported uranium oxides was prepared for the personnel of the project. It was recently indicated, however, that the information contained in that bibliography of abstracts be made more generally available, and the subsequent expansion of the original compilation has resulted in this publication.

The major source of the abstracts was from the excellent bibliography of Croxton,[3] which is not generally available.

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[1] R. F. Geller, A survey of ceramics for nuclear reactors, Nucleonics 7, 3 (1950).

[2] W. A. Lambertson, Ceramics and atomic energy, Bul. Am. Ceramic Soc. 30, 18 (1951).

[3] F. E. Croxton, Uranium and its compounds, a bibliography of unclassified literature, AEC Report No. K-295, Part 2 (March 1, 1951).

In addition, and mainly in an effort to make the bibliography current, such abstracting publications as Chemical Abstracts, Nuclear Science Abstracts, Technical Information Pilot (ONR, Library of Congress), and various individual journal publications have been reviewed from January 1, 1950, to June 30, 1952.

This annotated bibliography of unclassified and declassified AEC reports and of literature references is devoted to the high-temperature solid-state reactions (as opposed to the aqueous and solution chemistry reactions) of the uranium oxides (existing as such and not as chemical radicals) with other oxides. No special efforts were made to secure references on (a) any of the properties other than that of crystal structure, as determined by X-ray methods, and (b) on the reactions of the uranium oxides, other than UO_2 and U_3O_8, with other oxides. However, when information for other properties and reactions was readily available it was included. The major portion of the bibliography contains the known information on the reactions between uranium and oxygen for the formation, oxidation, and reduction of the various uranium oxides and their physical properties. A few references are given concerning the multitude of soluble uranium compounds and their numerous hydrated forms. Included are those which, when reacted with other compounds and calcined, resulted in the formation of one or more of the nonhydrated uranium oxides or a nonhydrated mixture or compound of one or more of the metallic oxides with one of the uranium oxides.

The abstracts given are not complete because they are not intended to be representative of the contents of the report. That is, they usually include only that material which has a direct bearing on the subject matter of this bibliography. Many of the original papers contain extensive discussions and descriptions of other related subjects. The abstracts are not evaluated. A number of borderline references are included, by title and reference only, at the end of each of the various categories.

For the convenience of the user, the Bibliography has been arranged chronologically and grouped into the following broad categories: reactions with uranium oxides; uranium oxides, general; UO_2; U_2O_5; U_3O_8; UO_3; and, uranium metal and miscellaneous reactions. Except for a few titles of dissertations all others in a foreign language have been translated into English.

For the first category of the Subject Index, references are given for the reactions of thirty-six oxides with one or more of the uranium oxides. Each of the next five categories have been subdivided into six broad classifications: general, crystal structure, preparation, properties, reactions (mainly oxidation and reduction), and additional references not abstracted. The abstracts have been cross-indexed.

It is hoped that the alphabetical Author Index will increase the usefulness of this work. There is included in the Appendix (1) a listing of the journal publication abbreviations, in general those used by Chemical Abstracts; and (2), a listing of the AEC numerical reports of the bibliography, both abstracted and listed by title only.

While every effort has been made to prepare this bibliography as completely and as accurately as possible, the author would greatly appreciate receiving information on errors and omissions which have occurred.

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BIBLIOGRAPHY

1. Reactions With Uranium Oxides

1.1 Uranates, peruranates, and polyuranates (1-55)

1. SOME EXPERIMENTS WITH URANIUM OXIDE AND ITS COMPOUNDS, J. J. Berzelius. Ann. Physik Chem. (Pogg.) **1**, 359 (1824).

   When K uranyl carbonate is ignited and the melt leached with water, an insoluble brick red power of $K_2U_2O_7$ is left behind. $K_2U_2O_7$ is only partially reduced by ignition in a stream of hydrogen. Method of preparing $BaO.2UO_3$, used by Arfvedson, will always contain $(NH_4)_2O.UO_3$ as an impurity. Substitute method using the preparation of uranyl nitrate with $Ba(OH)_2$ and washing of ppt. until no Ba is found is reported to yield a pure product.

2. SEPARATION OF SEVERAL METAL OXIDES, J. Persoz. Ann. chim. phys. **56**, 333 (1834).

   Preparation of $PbO.2UO_3$ from soln. of $UO_2(OAc)_2$ and basic lead acetate is reported.

3. REMARKS ON URANIUM, O. B. Kuhn. Ann. **41**, 337 (1842).

   Preparation of BaU_2O_7 by heating uranyl nitrate with a great excess of $Ba(OH)_2$.

4. ON URANIUM AND SOME OF ITS DOUBLE ACETATES, I. Wertheim. J. prakt. Chem. **29**, 209 (1843).

   When $K_2U_2O_7$ is reduced in hydrogen, material becomes violet-black but shown no change in crystalline form. Decomposes when ignited with oxalic acid in absence of air. When oxalic acid is not present, ignition of hydrated $K_2U_2O_7$ will produce anhydrous salt. Heating of magnesium uranyl acetate leaves a yellow-brown residue of magnesium uranate for which no formula is given. Ca and Sr uranyl acetates are reported to exist in analogous series with alkalies and alkaline earth uranyl acetates. When $BaO.2UO_3$ is prepared from uranyl acetate with $Ba(OH)_2$, a carbonate-free product is obtained. $PbO.2UO_3$ can be prepared from soln. of $UO_2(NO_3)_2$ and $Pb(NO_3)_2$ by pptn. with NH_3.

5. ON THE ANALYSIS OF ALKALI URANATES, F. Stolba. Z. anal. Chem. **3**, 71 (1864).

   Orange-yellow ppt. of $Na_2O.2UO_3$ obtained by treating UO_2SO_4 with excess NaOH. After drying in air this material has composition

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$Na_2O.2UO_3.6H_2O$. Ignition of hexahydrate produces anhydrous salt. $K_2U_2O_7$ can be pptd. from uranyl salt soln. with excess KOH, orange-yellow ppt. when dried in air is reported to have composition $K_2O.2UO_3.6H_2O$.

6. INVESTIGATIONS ON URANIUM. PRELIMINARY COMMUNICATIONS, J. L. C. Zimmermann. Ber. **14**, 440 (1881).

Crystalline $Na_2O.2UO_3$ is prepared by dissolving UO_2Cl_2, NaCl, and NH_4Cl in water, evaporating aqueous soln. and igniting residue. Material obtained is orange-yellow rhombic crystalline material, apparently isomorphous with corresponding K compound and with Li_2UO_4. Decomposes when ignited at white heat and completely reduced to UO_2 when heated in presence of hydrogen. Black residue from reduction shows no change in crystal structure. Crystals are not attacked by either hot or cold water, easily sol. in acid, even dil. HOAc. To prepare $K_2U_2O_7$, fresh UO_2Cl_2 is mixed with KCl and dissolved in water, evaporated to dryness. Residue is freed of NH_4Cl by gentle warming followed by ignition in Pt crucible until mass fuses, giving off strong fumes of KCl. As fusion continues, orange-yellow color is obtained which does not change when melt is cooled and reheated. Melt should be washed with water, orange-yellow crystalline residue dried at 100°C., and dehydrated by gentle heating. Will turn dark blood-red upon high heating but return to original color when cooled. Decomposes slightly at white heat, reduction to UO_2 is incomplete. Insol. in water and easily sol. in acids. Li_2UO_4 can be prepared in the same manner. Properties of lithium uranate are discussed particularly as regards its stability in relationship to the K and Na uranates. Lithium uranate turns brown when reduced by hydrogen although the crystal structure is not changed, is attacked by water after slight heating. Upon boiling loses orange color, gradually changing to yellow, apparently splitting compound into uranium and lithium hydroxides.

7. PRODUCTION BY THE DRY WAY OF SEVERAL CRYSTALLINE URANATES, A. Ditte. Compt. rend. **95**, 988 (1882).

Crust of Na_2UO_4 is formed on surface of melt of U_3O_8 and NaCl upon fusion in Pt crucible. Purification can be carried out by cooling and leaching with cold water. Na_2CO_3 is also valuable in the preparation. Brilliant green to golden-yellow flakes are obtained which are insol. in water, slightly sol. in dil. acids to yield a yellow soln., and do not melt at bright-red heat. K_2UO_4 can be prepared in same manner, as greenish-yellow flakes which fuse at bright-red heat. They are optically negative and insol. in water. Li_2UO_4 has approximately same properties as Na_2UO_4 and is prepared in same manner. $CaUO_4$ can be obtained very slowly by melting U_3O_8 with $CaCl_2$. Forms as small crystalline crust which can be separated from $CaCl_2$ by extraction with water. When pure, it is in form of yellow flakes. $Ca_2U_2O_7$ can be prepared by heating U_3O_8 with $Ca(ClO_3)_2$ and NaCl or $CaCl_2$. Material is formed as yellow-green flakes which are insol. in water but sol. in dil. acids. $BaO.2UO_3$ can be obtained in crystalline form by heating U_3O_8 with $Ba(ClO_3)_2$ similar to the preparation of the Ca salt. Crystallization is much faster. $BaUO_4$ is obtained in the same manner as the Ca salt. Crystallization is faster. Brilliant yellow-green plates which are sol. in hot dil. HCl are obtained. Study of crystallizations of $SrUO_4$ and $SrO.2UO_3$ are reported similar to Ca salts. $RbUO_4$ is obtained in same manner as sodium salt and has approximately same property. $MgUO_4$ is obtained by melting U_3O_8 with $MgCl_2$ or by heating with chlorate and adding $MgCl_2$. Extraction is accomplished with HCl and dark needles having a yellow tinge are obtained which are not affected by cold dil. HCl.

8. ON THE DECOMPOSITION OF PHOSPHATES AT HIGH TEMPERATURES BY POTASSIUM SULFATE, H. Grandeau. Compt. rend. **95**, 921 (1882).

K_2UO_4 prepared from uranyl phosphate by heating for several hours with KOH and excess K_2SO_4 between temperature of formation of KUO_2PO_4 and UO_3. Product usually can be isolated mechanically but is contaminated with other reaction products. Consists of fine orange-yellow flakes which appear hexagonal under microscope and are mostly rhombic in shape.

9. RESEARCH ON URANIUM, A. Ditte. Ann. chim. phys. **1**, 338 (1884).

Continuation of earlier work by author. Valuable early data on UO_2 and U_3O_8, Na, K, Li, Rb, Pb, Ca, Sr, Ba, and Mg uranates as well as Ba and Sr diuranates are discussed. Information on methods of preparation, physical properties, and appearance are included.

10. RESEARCH ON PHOSPHATES, H. Grandeau. Compt. rend. **100**, 1134 (1885).

KUO_2PO_4 prepared by heating $(UO_2)_3(PO_4)_2$ with excess K_2SO_4 and K_2O. Double phosphate decomposes in presence of alkali forming

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K_2UO_4. K_2UO_4 prepared from uranyl phosphate by heating for several hours with excess K_2SO_4 between temperature of formation of potassium uranyl phosphate and UO_3. Consists of fine orange-yellow flakes which appear hexagonal under microscope.

11. OF THE ACTION OF POTASSIUM SULFATE AT HIGH TEMPERATURES ON METALLIC PHOSPHATES, H. Grandeau. Ann. chim. phys. 8, 193 (1886).

Double phosphate, KUO_2PO_4, when combined with alkali, forms the uranate, K_2UO_4. Uranate is usually contaminated with other reaction products. Consists of fine orange-yellow flakes.

12. UEBER URANSAURE UND DEREN SALZE, V. Fischel. Dissertation, Univ. of Bern, 1889.

$K_2U_2O_7$ can be obtained from uranic acid mixed with KCl and ignited strongly for two hours. Melt which becomes a grayish-brown gradually changes to orange-yellow, then boiled with water and dried. Li_2UO_4 can be prepared in the same manner as K_2UO_4. $Na_2U_2O_7$ prepared by igniting mixture of pptd. uranic acid and NaCl for two hours in blast lamp, boiling residue with water to leach out impurities, drying at 100°C. BaU_2O_7 obtained by short intense heating of uranic acid with $BaCl_2$. Purification is similar to that for $K_2U_2O_7$. Crystallization of $MgUO_4$ reported with brown, irregular and amorphous materials being obtained. CaU_2O_7 obtained by heating uranic acid with $CaCl_2$. Crystallization of SrU_2O_7 is analogous to corresponding Ca salt; however, proceeds at slower rate. When freshly pptd. uranic acid is heated to dull-red heat with slight excess $BiCl_3$, silky brick-red crystals of composition $2Bi_2O_3.3UO_3$ or $(BiO)_4U_3O_{11}$ are formed. Excess $BiCl_2$ is volatilized by prolonged heating.

13. CRYSTALLOGRAPHIC AND OPTICAL STUDY OF NEUTRAL URANATE AND ANHYDROUS SODA, L. Michel. Bull. soc. franc. mineral. 13, 72 (1890).

Na_2UO_4 prepared by decomposition of uranium molybdate with NaCl is in form of brilliant, reddish-yellow, transparent, rhombic prisms which are strongly birefringent.

14. ON SODIUM PEROXIDE AND ITS USE IN ANALYSIS, O. Kassner. Arch. Pharm. 232, 226 (1894).

$Na_2O.2UO_3$ can be obtained by prolonged boiling of a yellow soln. of $Na_4UO_8.8H_2O$.

15. ON SODIUM PEROXIDE, T. Poleck. Ber. **27**, 1051 (1894).

$Na_2O.2UO_3$ can be obtained by prolonged boiling of a yellow soln. of $Na_4UO_8.8H_2O$.

16. INVESTIGATIONS ON NIOBIUM, A. Larsson. Z. anorg. Chem. **12**, 188 (1896).

Melt of U-niobate in boric acid yields a number of different compounds, among them a yellow tabular crystal which could not be satisfactorily analyzed but which was supposed to be $3UO_3.B_2O_3$.

17. ON URANIC ACID AND ITS SALTS, P. G. Melikoff and L. Pissarjewsky. Ber. **30**, 2902 (1897).

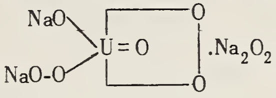
Structure of peruranates is discussed and peroxide formula $R_2U_2O_{10} = R_2O_2.2UO_4$ and $R_4UO_8 = 2R_2O_2.UO_4$ is proposed. Preferred since substances can be characterized as compounds of metallic peroxides with UO_4.Na_4UO_8 obtained by dissolving hydrated UO_3 or UO_4 in excess NaOH and adding H_2O_2. Compound crystallizes in hydrated form from conc. soln. after few hours, or from dil. soln. upon addition of alcohol. Crystalline cubes are isotropic. Red crystalline compound of formula Li_4UO_8 was obtained, but material is very unstable, losing oxygen when allow to stand over sulfuric acid. $BaU_2O_{10}.9H_2O$ is obtained as flocculent pptd. in same manner as corresponding ammonia salt. When dried over sulfuric acid and soda lime, yellow crystalline powder results. Decomposes in presence of CO_2. $BaUO_8.8H_2O$ is obtained in the same manner as corresponding Na salt, using $BaCl_2$. Orange, powderlike crystals result after drying ppt. over sulfuric acid and soda lime. Dark-orange lead peruranate, $Pb_3U_2O_{10}$, is obtained by mixing soln. of $Na_2U_2O_7$ and $Pb(OAc)_2$ and drying ppt. over sulfuric acid and soda lime. Occurs in form of small isotropic prisms which are decomposed by sulfuric acid with separation of H_2O_2. Calcium peruranate, $Ca_2UO_8.10H_2O$, is formed as ppt. of pale-yellow crystals by decomposition of the corresponding soda salt with $CaCl_2$. Crystals decompose with sulfuric acid by separating H_2O_2.

18. PERURANIC ACID AND ITS SALTS, P. G. Melikoff and L. Pissarjewsky. Zhur. Russ. Fiz. Khim. Obshchestva **30**, 103 (1898).

Structure of peruranates is discussed and proposed that peroxide formula $R_2U_2O_{10} = R_2O_2.2UO_4$ and $R_4UO_8 = 2R_2O_2.UO_4$ is preferred since substances can be characterized as compounds of metallic peroxides with UO_4. See also Bull. soc. chim. France **22**, 8 (1899).

19. THE SALT OF PYROPERVANADIC ACID AND THE CONSTITUTION OF ITS ACID SALT, P. Melikoff and L. Pissarjewsky. Z. anorg. Chem. **19**, 405 (1899).

Comparisons made with similar salts of Mo, U, and W. Structures for pyrouranic acid salts are given. Structural formula



assigned to Na_4UO_8.

20. ON URANIC, ON MOLYBDIC, AND ON WOLFRAMIC ACIDS AND CORRESPONDING ACIDS. THERMOCHEMICAL INVESTIGATION, L. V. Pissarjewsky. Z. anorg. Chem. **24**, 108 (1900).

Heat of reaction for $UO_3.H_2O + H_2O = UO_4.2H_2O$ calculated as -6151 cal. Na_4UO_8 crystallizes with 9 molecules water. $UO_3.\frac{1}{2}H_2O$, or $H_2U_2O_7$, is formed somewhat above 160°C. at water-vapor pressure of 15 mm Hg. At 300°C. goes to anhydrous UO_3. Heat of neutralization for one mole of material by 2 moles of NaOH is +17.859 kcal. Heat of reaction liberated in decomposition of Na_2UO_8 with sulfuric acid is 36,497 cal.

21. ON INDIUM, C. Renz. Ber. **34**, 2763 (1901).

Indium uranate can be prepared by pptn., using soln. of In chloride with Na_2UO_4.

22. ON THE NATURE OF CERTAIN SODIUM URANIUM COMPOUNDS, F. J. Metzger and M. Heidelberger. J. Am. Chem. Soc. **31**, 1040 (1909).

Investigation to determine whether product obtained in analysis of U by Patera's method was correctly represented by formula $NaO(U_2O_3)_2$. Samples of Na uranate were prepared and Na-U ratio determined. Same ratio also determined for Patera's ppt. Results show that ratio of Na to U in Na uranate was 4:5.17 instead of 1:1, thus making analytical formula $Na_4U_5O_{17}$. For Patera's ppt. formula was $Na_9U_{11}O_{35}$. While Na uranate may actually be pptd. as $Na_2U_2O_7$, completely removing excess alkali by washing with water, ppt. undergoes partial hydrolysis or reversal of reaction by which it was formed, extent depending upon amount of washing and upon certain physical constants not determined.

23. THE ANALOGY BETWEEN URANIUM AND OTHER ELEMENTS, F. W. Oechsner de Coninck. Bull. classe sci. Acad. roy. Belg. 175, (1909).

Uranates of type R_2UO_4, diuranates of type $R_2U_2O_7$, and peruranates of type R_2UO_5 were found to form many combinations with oxides and especially with alkali and oxides of alkaline earths. These are analogous to compounds, as well as somewhat similar to pyroacids, of P, Sb, and Bi in higher condition of oxidation.

24. CONTRIBUTIONS TO THE STUDY OF URANYL CHLORIDE, F. W. Oechsner de Coninck. Compt. rend. **148**, 1769 (1909).

UO_2Cl_2 is reduced by hydrogen with heat to UO_2 and HCl. Crystals heated in open tube with an excess of KOH form red perurانate, K_2UO_5, which slowly loses oxygen, giving K_2UO_4. Yellow $BaUO_4$ is pptd. from UO_2Cl_2 by $BaCl_2$.

25. THE PREPARATION OF URANATES IN THE WET WAY, F. W. Oechsner de Coninck. Bull. classe sci. Acad. roy. Belg. 835 (1909).

UO_2Cl_2 in dil. soln. was treated with $BaCl_2$, $SrCl_2$, $CaCl_2$, or $MgCl_2$ in sol. before adding NH_4OH free from carbonate. Uranates were pptd. as the hydrates. They can then be dried to anhydrous salts.

26. A STUDY OF THE URANATES, F. W. Oechsner de Coninck. Bull. classe sci. Acad. roy. Belg. 173 (1909).

Uranates, in general, correspond to formula R_2UO_4. When UO_2Cl_2 was fused with KOH in presence of O_2, K_2UO_5 was obtained. Heated to fusion with KOH, O_2 was evolved and K_2UO_4 remained. Pure K_2UO_5, Na_2UO_5, and $BaUO_5$ were prepared and analyzed. $CaUO_5$ was obtained, impure, with $CaUO_4$. Salts vary in color from red to orange and yellow.

27. URANOUS OXIDE, F. W. Oechsner de Coninck. Bull. classe sci. Acad. roy. Belg. 744 (1909).

K and Na react with UO_2Cl_2 to give UO_2 contaminated with alkaline uranate; Mg and Al react to give UO_2. CaO and $Ba(OH)_2$ react with UO_2Cl_2 to give UO_2; CuO reacts to give UO_2 with a small amount of copper uranate.

28. EINWIRKUNG VON TROCKEM AMMONIAK AUF WASSERFREIE URANYLSALZE, A. vonUnruh. Dissertation, Univ. of Rostock, 1909.

$Na_2O.2UO_3$ obtained when Et_2O soln. of $UO_2(NO_3)_2$ treated with metallic Na. Decomposition of $UO_2(NO_3)_2.3H_2O$ yields orange-red UO_3, which is formed at 250° to 300° C. $CaO.2UO_3$ was formed using CaO. Impossible to ppt. anhydrous $UO_2(NO_3)_2$ from soln. of AmOH.

29. UEBER PEROXYURANATE, J. G. Zahn. Dissertation, University of Frieburg, 1912.

29--Continued

Dissertation includes considerable information on properties of peruranates; colors: $R_2U_2O_{10}$, light green to light-yellow; R_2UO_6, reddish-yellow to brownish-red; R_3UO_7 or $R_6U_2O_{13}$, yellow to brown; R_4UO_8, yellow to dark-red; and compounds of R_4UO_8 with H_2O_2, light-green and extremely explosive. Most peruranates turn red in air and take up water, all turn red upon ignition. Each is sol. in water, least sol. compounds are $R_2U_2O_{10}$. All are sol. in dil. acids except HOAc which quantitatively ppts. white U peroxide. Considerable discussion on the hydrated alkali peruranates.

30. MAGNESIUM CHLORIDE AS A MINERALIZER, WITH SOME REMARKS ON THE SPECTRO-CHEMISTRY OF THE RARE EARTHS, K. A. Hofmann and K. Hoschele. Ber. 47, 238 (1914).

$3MgO.2UO_3$ obtained by melting UO_3 in $MgCl_2$ and washing. Double refractive prisms are obtained which are sol. in dil. HOAc.

31. REMAINDER ON REACTIONS BETWEEN CoO AND VARIOUS METAL OXIDES AT HIGH TEMPERATURES, J. A. Hedvall. Z. anorg. allgem. Chem. 93, 313 (1915).

When mixture of CoO and UO_3 are heated at 1,100° to 1,300° C., a crystalline yellow cobalt uranate is formed.

32. MAGNESIUM CHLORIDE AS A MINERALIZER. II. URANIUM-CERIUM BLUE AND THE NATURE OF CONSTITUTIVE COLORING. MAGNESIUM RED AND MAGNESIUM GREEN, K. A. Hofmann and K. Hoschele. Ber. 48, 20 (1915).

Anhydrous molten $MgCl_2$ is excellent crystallizing medium for many inorganic oxides. Heating 5 parts $Ce_2(SO_4)_3$ and 2 parts of $UO_2SO_4.31/2\ H_2O$ with excess $MgCl_2$ for 15 hours over Teclu burner caused formation of dark-blue double oxide of CeO_2 and UO_2 in the ratio 2:1. Colorless $Ce(OH)_3$ is pptd. from Ce salts by NH_4OH, reddish-brown flakes of $U(OH)_4$ are pptd. from soln. of U salts by NH_4OH. If excess NH_4OH is added to soln. containing both salts, yellowish ppt. is formed which in 10 to 20 min. forms a compact, deep-blue ppt. Deep-blue oxide is a compound, not a mixture. Compound has same composition, other than water content, as blue oxide obtained from $MgCl_2$ melt. Change in color is due to change in state of oxidation of atoms within molecule under influence of light. In Ce-U blue there is an oscillating change in state of oxidation, $Ce^{+4}\text{-}Ce^{+4}O_6U^{+4} \rightleftarrows Ce^{+3}\text{-}Ce^{+3}O_6U^{+6}$.

33. ACTION OF ULTRAVIOLET RAYS ON MINERAL COMPOUNDS. SECOND COMMUNICATION, E. Montignie. Bull. soc. chim. France 45, 708 (1929).

33—Continued

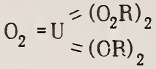
Potassium uranate (for which no formula is given) is not attacked when irradiated for 1 hour with ultraviolet rays. When U_3O_8 is treated with ultraviolet light and placed in contact with photographic plate, strong effect will be found as long as 5 days after irradiation.

34. FURTHER ACTION OF MAGNESIUM AMALGAM ON NITRATES AND ITS ACTION ON NITROUS ACID, AND SALTS OF THE OXYACIDS OF SULFUR AND THE HALOGENS, P. Neogi and R. C. Bhattacharyya. J. Indian Chem. Soc. 6, 333 (1929).

Impure uranium hyponitrite was prepared by treating uranium nitrate soln., cooled in ice salt bath, with 5% Mg amalgam. Yellow PbU_2O_7 was obtained by treating soln. with $Pb(NO_3)_2$.

35. PERMOLYBDATES AND PERTUNGSTATES AND THE STRUCTURE OF PERCHROMATES, A. Rosenheim, M. Hakki, and O. Krause. Z. anorg. allgem. Chem. **209**, 175 (1932).

Structure of perchromates, permolybdates, pertungstates, and peruranates discussed, and structural formula



$$O_2 = U \begin{smallmatrix} \diagup (O_2R)_2 \\ \diagdown (OR)_2 \end{smallmatrix}$$

thought probable for peruranates.

36. THE CRYSTAL STRUCTURE OF BARIUM URANATE; THE NONEXISTENCE OF THE UO_4 GROUP, S. Samson and L. G. Sillen. Arkiv Kemi, Mineral. Geol. **A25**, No. 21, 1947.

Tabular golden-yellow single crystals of $BaUO_4$ were prepared by fusion of $(NH_4)_2U_2O_7$ in 8-fold excess of $BaCl_2$. X-ray diffraction diagrams registered (including Weissenberg photographs of zero, first, and second layers) about (001) and (010). Heavy atoms located by Fourier methods, and O atoms placed by space and symmetry considerations. Cell dimensions are $a = 5.751$, $b = 8.135$, $c = 8.236$ A, all ± 0.005A, with 4 molecules per unit cell. Space group is D_{2h}^{11}-Pbcm. 4 Ba are in 4(d), $x = 9.474$, $y = 0.200$; 4 U are in 4(a); 8 O^1 are in 8(e), $x = 0.29$, $y = -0.06$, $z = 0.09$; 4 O^2 in 4(c), $x = 0.11$; and 4 O^3 in 4(d), $x = -0.13$, and $y = -0.04$. Structure consists of infinite layers parallel to (100) of octahedrally coordinated U atoms, linked in layer by 4 shared corners. Each U atom associated with 2 unshared O atoms. Ba ions bind separate layers.

36—Continued

Slight solubility of uranates attributed to this silicate-like coordination.

37. X-RAY DIFFRACTION STUDIES OF MISCELLANEOUS URANIUM COMPOUNDS, W. H. Zachariasen. MDDC-1152, June, 1946; declassified July 18, 1947.

Lattice dimensions are given for K_2UO_4 and $BaUO_4$. Positions of heavy-metal atoms have been found for most compounds. Summary of results of incomplete crystal structure determinations for miscellaneous U compounds is given.

38. CRYSTAL STRUCTURE OF BARIUM URANATE: THE ABSENCE OF UO_4 GROUPS, S. Samson and L. G. Sillen. Arkiv Kemi, Mineral. Geol. A25, paper no. 21, 1948.

U differs from related Cr, Mo, and W in that all uranates are insol. while alkaline chromates, molybdates, and tungstates are, as a rule, readily sol. Assumed this difference related to increasing radii of 6-valent ions, from Cr to U; whereas, CrO_4 groups are probably well developed in chromates and corresponding tetrahedra show certain deformations in molybdates and tungstates, radius of U^{+6} ion must be too large to allow stable tetrahedra grouping of O ions. Assumptions tested on $BaUO_4$ (was proposed to use BaU_2O_7). Complete lattice determination was made, confirming predicted absence of UO_4 groups. Structure should account for nonsolubility of uranates.

39. THE CRYSTAL STRUCTURE OF $CaUO_4$ AND $SrUO_4$, W. H. Zachariasen. Acta Cryst. 1, 281 (1948).

Isomorphous compounds $CaUO_4$ and $SrUO_4$ were prepared by adding U_3O_8 to molten $CaCl_2$ or $SrCl_2$. Deduction of chemical formulas from x-ray diffraction data is described.

40. NEW STRUCTURAL TYPES WITH DENSEST PACKING OF CONSTITUENT ATOMS, N. V. Belov. Dokaldy Akad. Nauk S.S.S.R. 65, 677 (1949).

Recently published determinations of crystal structure of heavy-element compounds, in particular those containing uranium and transuranium elements [(Zachariasen, Acta Cryst. 1, 265 (1948); Aurivilius, Arkiv Kemi Mineral. Geol., 26B, No. 2, (1948)], fit very well systematics proposed by author in book "Structure of ionic crystals and metallic phases," Moscow-Leningrad, 1947. $CaUO_4$ is one case discussed. Leading idea of systematics is densest possible packing of large ions, principally anions.

41. ALKALINE EARTH POLYURANATES, H. R. Hoekstra and J. J. Katz. AECD-2647, June 1949; declassified July 12, 1949.

Preparation of alkaline earth polyuranates is critically discussed. Thermal decomposition of double alkaline earth uranyl acetates provides simplest approach to synthesis of compounds. MgU_2O_7 undergoes reversible decomposition at elevated temperatures. Equilibrium studies of decomposition are described, and phase relationships are discussed. Preliminary observations on dissociation of the Ca, Sr, and Ba compounds are discussed. Includes diuranates of Mg, Ca, Sr, and Ba.

42. ABSORPTION SPECTRA OF THE SODIUM PERURANATES, T. V. Arden and P. McGlone. Nature, **166**, 560 (1950).

Presence of bicarbonate in soln. of sodium peruranate formed by addition of excess hydrogen peroxide to sodium uranyl tricarbonate soln. causes errors in absorptionmetric determination of uranium. Absorption spectra of soln. of uranium trioxide in sodium carbonate and excess sodium hydroxide, in sodium carbonate, in equal quantities of sodium carbonate and sodium bicarbonate, and in sodium bicarbonate (a large excess of hydrogen peroxide being present in each case) were determined. Changes in absorption spectra are due largely to changes in proportions of three peruranates, Na_2UO_6, Na_4UO_8, and $Na_2U_2O_{10}$, effect of absorption by $Na_4UO_2(CO_3)_3$ being relatively unimportant.

43. THE CONSTITUTION OF THE URANATES OF SODIUM, C. A. Wamser, J. Belle, E. Bernsohn, and B. Williamson. AECD-2933, declassified Aug. 2, 1950.

Chemical and x-ray diffraction analyses and interpretation of pH and conductivity data indicate that two uranates, $Na_2U_7O_{22}$ and $Na_6U_7O_{24}$ (or mixtures thereof) are obtained in the pptn. of uranate with NaOH from $UO_2(NO_3)_2$ soln.

44. MAGNETIC SUSCEPTIBILITIES OF URANIA-THORIA SOLID-SOLUTIONS, W. Trzebiatowski and P. W. Selwood. J. Am. Chem. Soc. **72**, 4504 (1950).

Magnetic moment of tetravalent uranium was determined in solid-solutions of uranium dioxide with dimagnetic thorium dioxide in concentration range 100 to 2% urania. Molar susceptibility of uranium rises sharply with increasing magnetic dilution, but is caused almost entirely by diminution of the Weiss constant. Magnetic moment of uranium shows little, if any, dependence on concentration. Moment at greatest dilution is in agreement with "spin

44—Continued

only'' formula for two unpaired electrons, and hence with 6d rather than 5f electron distribution.

45. THE OXIDES OF URANIUM. PART II: BINARY SYSTEM UO_2-CaO, K. B. Alberman, R. C. Blakey, and J. A. Anderson. J. Chem. Soc. (London) **26**, 1352 (1951).

System was investigated in temperature range from 1650° to 2300° C, eutectic temperature is 2080° ±20° C at about 45 mole % UO_2 and 55 mole % CaO. CaO takes no detectable amount of UO_2 into solid-solution, but UO_2 forms solid-solutions, with defective fluorite structure; saturated solid-solution contains 47 mole % CaO at eutectic temperature. Concentration of CaO in saturated solid-solution decreases with falling temperature, 20 mole % at 1650°C. At 1750°C and below, two compounds are formed: Ca_2UO_4 ($2CaO.UO_2$), tetragonal double oxide of unknown structure; and $CaUO_3$ ($CaO.UO_2$), cubic, $a = 10.727 \pm 0.002$ kX. Structure of latter is equivalent to Type-C rare-earth oxide structure, with $Ca^{2+} + U^{4+}$ replacing $2M^{3+}$. Compound $CaUO_3$ is completely indexed in terms of rare-earth Type-C structure, and partially indexed in terms of fluorite cell, containing 16 molecules $CaUO_3$ per unit cell. Compound Ca_2UO_4, diffraction pattern indicated tetragonal cell with at least one rather large dimension; measurements could be indexed in terms of cell, $a = 16.760$, $c = 9.208$ kX, $c/a = 0.549$, containing 32 molecules Ca_2UO_4 in conformity with Zachariasen's data for spatial requirements of Ca^{2+}, O^{2-}, and U^{4+}.

46. A STUDY OF EQUILIBRIUM PHASES IN THE SYSTEM UO_2-ZrO_2, W. A. Lambertson and M. H. Mueller. AECD-3068, Jan. 1951, declassified Feb. 27, 1951.

Phase-equilibrium studies reveal that system consists primarily of two solid-solutions separated by a two-phase region which decreases in area as temperature is increased. UO_2 solid-solution is cubic, extending from 0 to 40% ZrO_2 by weight, lattice parameter varies from 5.460 to 5.277 kX with increasing ZrO_2. ZrO_2 solid-solution is tetragonal, extending from 50 to 100% ZrO_2, lattice parameters vary: a_0 from 5.23 to 5.07 kX and c_0 from 5.27 to 5.16 kX. Evidence of a solid-solution in monoclinic ZrO_2.

47. ON THE CERIUM DIOXIDE-URANIUM DIOXIDE SYSTEM AND "URANIUM CERIUM BLUE," A. Magneli and L. Kihlborg. Acta Chem. Scand. **5**, 578 (1951).

47—Continued

Dark-blue cubic crystals of cerium uranium oxide obtained by Hoffman et al [Ber. **48**, 20 (1915)] were considered definite chemical compound $2CeO.UO_2$. By studying X-ray powder photographs of substance established that "cerium uranium blue" can be of variable composition, forming a continuous series of solid-solutions, $(Ce, U)O_2$, of fluorite-type lattice.

48. THE FLUORITE PHASE IN THE U_3O_8-Er_2O_3 SYSTEM, F. Hund and U. Peetz. Z. anorg. allgem. Chem. **267**, 189 (1952).

Fluorite phase was observed between 27.0 and 66.7 mole % Er_2O_3, lattice constant varied linearly from 5.349 ± 0.001 to 5.303 ± 0.001 A at Er-rich end. Pycnometric densities compared with values calculated for both anion and cation defective lattice types. Structure of mixed crystals is that of ideal cation lattice with excess anions in interlattice positions or with vacancies in anion partial lattice. Some considerations on structure of U_3O_8 and Er_2O_3 are given by extrapolated lattice constants.

49. STUDIES ON THE ALKALINE EARTH DIURANATES, H. R. Hoekstra and J. J. Katz. J. Am. Chem. Soc., **74**, 1683 (1952).

All six methods reported in literature investigated for preparation of alkaline earth diuranates. Ignition of metal uranyl acetate was only one to give a pure product free of excess of either alkaline earth metal or uranium oxide. Magnesium and barium uranyl acetates were easily obtained pure but preparation of calcium and strontium salts caused difficulty because of high solubilities and marked tendency for uranyl acetate to coprecipitate with desired double acetate. Double acetates were prepared, using C. P. reagents without further purification, as follows: uranyl acetate and alkaline earth acetate (in 2:1 molar ratio) were dissolved in minimum volume of 4M acetic acid at 80°. Soln. was centrifuged while hot to remove traces of insol. impurities, then cooled to 0°. If double acetate did not ppt. on standing, the soln. was allowed to evaporate at room temperature until pptn. did occur. Yellow crystals of double acetate were filtered, washed with cold 4M acetic acid, and dried at 60°. Analyses were made for alkaline earth metal and uranium. Magnesium and calcium uranyl acetates prepared were hexahydrates, strontium and barium salts were dihydrates. Acetates were heated slowly in air to 700° to form diuranates, which were also analyzed. Color of diuranates were: magnesium—dull orange; calcium—light orange with greenish tinge; strontium—orange; and, barium—bright orange. Analyses were made gravimetrically by conventional methods: uranium was separated as peroxide, pptd. with ammonia before ignition to U_3O_8; magnesium was pptd. as magnesium ammonium phosphate and weighed as pyrophosphate; calcium pptd. as oxalate and ignited to oxide; and strontium and barium pptd. and weighed as sulfates. Thermal stability of metal diuranates in vacuum and in oxygen at temperatures up to 1100° was investigated by tensimetric methods. Metal diuranate-oxygen systems found to be reversible below 1100°. Equilibria dissociation pressures of oxygen so obtained permit outlining diphasic and monophasic regions of composition encountered, calculation of decomposition isotherms and isobars, and heats of reaction, free energy changes and entropy changes involved. Qualitative studies on rates of oxidation of decomposition products to diuranates were made. X-ray investigation of solids of composition MeU_2O_6 indicate structrual similarity to uranium dioxide. Magnesium diuranate consists of two solid phases, $MgUO_4$ and MgU_3O_{10}. Samples in magnesium diuranate system with the empirical formulas $MgU_2O_{6.04}$ and $MgU_2O_{5.90}$ were found to have fluorite structure of uranium dioxide, but with smaller unit cell (5.281 A for 6.04 and 5.292 A for 5.90). MgU_2O_6 structure intrepreted as uranium dioxide (fluorite) structure with every third uranium atom replaced by magnesium. Relatively smaller size of unit cell ascribed to smaller magnesium ion and to existence of uranium in pentavalent state rather than tetravalency it exhibits in UO_2. Calcium and strontium compounds having formula MU_2O_6 also exhibit fluorite structure with unit cell size increasing with size of alkaline earth atom, i.e., CaU_2O_6, 5.379 A, and SrU_2O_6, 5.452 A. Densities of solids calculated from X-ray data are: MgU_2O_6, 8.97 g/cm^3; CaU_2O_6, 8.71 g/cm^3; and SrU_2O_6, 9.07 g/cm^3.

50. ON CERIUM-URANIUM BLUE AND THE SEMICONDUCTIVE PROPERTIES OF THE MIXED-CRYSTAL SERIES UO_2-CeO_2, W. Rudorff and G. Valet. Z. Naturforsch. **7b**, 57 (1952).

Series of pure CeO_2-UO_2 mixed crystals prepared by igniting Ce(IV) and U(IV) salts at 1200°C in high vacuum, all crystals were blue. Specific resistance of UO_2, 5×10^3 ohm-cm, decreased with CeO_2 additions to minimum of 2.5×10^2 ohm-cm at 40 mole % CeO_2. High conductivity is explained by electron exchange between valence states. Contrast is drawn with behavior of brown UO_2-ThO_2 mixed crystal series.

51. THE EQUILIBRIA OF PARTIAL BINARY SYSTEMS OF UO_2 WITH Al_2O_3, BeO, MgO, and SiO_2. PART I—THE SYSTEM UO_2-Al_2O_3, S. M. Lang, C. L. Fillmore, and R. S. Roth, NBS Interim Report to AEC, 1952.

When oxygen content is reduced to one part in at least three million parts of protective helium atmosphere, there are no compounds, solid-solubilities, nor any other solid-state reactions present at temperatures from 800° to 1800°C within compositional range from 10 to 90 mole % of UO_2. Binary eutectic may be at about 20 mole % UO_2 and about 1800° ± 50°C (from visual observation of heated X-ray samples).

52. THE EQUILIBRIA OF PARTIAL BINARY SYSTEMS OF UO_2 WITH Al_2O_3, BeO, MgO, and SiO_2. PART II—THE SYSTEM UO_2-BeO, S. M. Lang, C. L. Fillmore, and R. S. Roth, NBS Interim Report to AEC, 1952.

When oxygen content is reduced to one part in at least three million parts of protective helium atmosphere, there are no compounds, solid-solubilities, nor any other solid-state reactions present at temperatures from 800° to 1800°C within compositional range from 10 to 90 mole % of UO_2.

53. THE EQUILIBRIA OF PARTIAL BINARY SYSTEMS OF UO_2 WITH Al_2O_3, BeO, MgO, and SiO_2. PART III—THE SYSTEM UO_2-MgO, S. M. Lang, C. L. Fillmore, and R. S. Roth, NBS Interim Report to AEC, 1952.

When oxygen content is reduced to one part in at least three million parts of protective helium atmosphere, there are no compounds, solid-solubilities, nor any solid-state reactions present at temperatures from 400° to 1800°C within the compositional range from mole ratio $4UO_2$:1MgO (about 96 wt. % UO_2) to mole ratio $1UO_2$:50MgO (about 12 wt. % UO_2).

54. THE SYSTEM U_3O_8-MgO. PRELIMINARY STUDY, S. M. Lang, C. L. Fillmore, and R. S. Roth. NBS Interim Report to AEC, 1952.

General survey indicates transition temperature at about 900° to 1000°C for solid-state reactions involving at least three unknown crystalline phases, equilibrium conditions at elevated temperatures requiring at least two weeks. Under prolonged heating (above about 1300°C) in oxidizing atmospheres U_3O_8 decomposes to a lower oxide, eventually to UO_2.

55. THE EQUILIBRIA OF PARTIAL BINARY SYSTEMS OF UO_2 WITH Al_2O_3, BeO, MgO, and SiO_2. PART IV—THE SYSTEM UO_2-SiO_2, S. M. Lang, C. L. Fillmore, and R. S. Roth, NBS Interim Report to AEC, 1952.

When oxygen content is reduced to one part in at least three million parts of protective helium atmosphere, there are no compounds, solid-solubilities, nor any other solid-state reactions present at temperatures from 800° to 1600°C within the compositional range from 10 to 90 mole % UO_2. Binary eutectic may be at approx. 1600° ± 50°C (from visual observations of heated X-ray samples).

1.2 Complex uranates, peruranates, and polyuranates

None.

1.3 Additional references not abstracted

"On the composition of a group of uranium silicate minerals," R. Hermann. J. prakt. Chem. **76**, 320 (1859).

"On the composition of a group of uranium silicate minerals," R. Hermann. Bull. soc. imp. naturalistes Moscou **32**, 107 (1859).

"On the composition of a group of uranium silicate minerals," R. Hermann. Arch. wiss. Kunde Russ. **19**, 265 (1860).

"On a uranium-containing mineral from the Moss region and on native uranates in general," C. W. Blomstrand. J. prakt. Chem. **29**, 191 (1884).

"On the native uranates," C. W. Blomstrand. Ann. chim. phys. **4**, 129 (1885).

"On a uranium containing mineral from the Moss region and on native uranates in general," C. W. Blomstrand. Geol. Foren. i Stockholm Forh. **7**, 59 (1885); ibid, page 196.

"Zur Kenntnis der Peruransaure und Peruranate," H. Daehr. Berlin, 1928.

"Potassium uranates," R. Flatt and W. Hess. Helv. Chim. Acta. **21**, 1506 (1938).

2. Uranium Oxides, General (300-336)

300. THE CHEMICAL INVESTIGATION OF URANITE, A NEWLY DISCOVERED METALLIC SUBSTANCE, M. H. Klaproth. Chem. Ann. (Crell) II, 387 (1789).

Reports first preparation of UO_2 although at that time was believed to be element rather than oxide. UO_2 was prepared by reduction of UO_3 in a C crucible. Method of analysis (for UO_2) is given.

301. RESEARCH ON URANIUM, E. Peligot. J. prakt. Chem. **24** (1) 442 (1841).

Identification of UO_2 (as prepared by Klaproth) as oxide and not metal as assumed.

302. RED URANIUM COMPOUNDS, A. Parera. Ber. Mitt. Freund. Naturw. Wein. **5**, 45 (1849).

Ammonium uranium red obtained as blood-red ppt. from uranyl soln. when treated with $(NH_4)_2S$ and reaction mixture allowed to stand in presence of air for from one to two days. Substance can be dissolved in acids, evolving H_2S and free S. NH_3 can be displaced by other bases upon boiling with alkali or alkaline earth hydroxide. Sodium uranium red can be pptd. from uranyl soln. using H_2S and NaOH; no further investigation was made. Potassium uranium red is obtained from ammonium uranium red by boiling with KOH solution.

303. RESEARCH ON THE SULFUR COMPOUNDS OF URANIUM, A. Remele. Ann. Physik Chem. (Pogg.) **125**, 209 (1865).

Uranium red consists of mixture of uranyl hydroxide with red modification of UO_2S. Ammonium U red obtained as blood-red ppt. from uranyl salt soln. when treated with $(NH_4)_2S$ and reaction mixture allowed to stand in air for from one to two days. See also: "On uranium red." A. Remele. Mondes, **6**, 459 (1864).

304. STUDY OF HYDROGEN DIOXIDE AND CERTAIN PEROXIDES, INCLUDING EXPERIMENTS TO DETERMINE THE HEAT OF FORMATION OF THE OXYGEN MOLECULE, T. Fairley. J. Chem. Sec. **31**, 125 (1877).

Anhydrous peroxide, UO_4, obtained when mixture of H_2O_2 and uranyl nitrate was treated with great excesses H_2SO_4 and allowed to stand for long time. Unsuccessful attempts to prepare UO_4 by strong oxidation of acidic, neutral, or alk. soln. of uranic acid and uranates reported. $UO_4.2H_2O$ can be formed as a yellowish-white ppt. when pure dil. H_2O_2 is added to soln. of uranyl nitrate or acetate. Material is stable in presence of excess uranyl salts and can be dried at 100°C without losing H_2O or O_2. When H_2O_2 is used in excess, O_2 is lost during filtration, especially when mother liquor is still warm. Formula for UO_4, although it forms wide variety of peruranates, is proposed to be $2UO_3.UO_6.6H_2O$. These peruranates can be regarded as salts of $UO_4.2H_2O$; however, in view of behavior with alk., are usually formulated as triple molecules, in which one or more UO_3 groups may be replaced by an alkali. Peroxide formula showing that type of linkage for peruranates is proposed.

305. ON THE DECOMPOSITION AND TRANSFORMATION PRODUCT OF URANYL SULFIDE, J. L. C. Zimmermann. Ann. **204**, 204 (1880).

Discussion of pptn. of U from soln. using carbonate-free $(NH_4)_2S$. Pptn. beaker must be kept at 100°C until soln. is clear. Same results are obtained using NH_4OH. Potassium uranium red can be prepd. quickly by treating U salt soln. with freshly prepd. potassium hydrosulfide and boiling the ppt. in excess reagent. Refutes contention of Remele that uranium red consists of mixt. of uranyl hydroxide and uranyl sulfide. Suggests, instead, formula $2UO_3.UO_2(OK)SK$ for K red. Ammonium uranium red can be obtained as blood-red ppt. from uranyl salt soln. when treated with $(NH_4)_2S$ and reaction mixture allowed to stand in presence of air for from one to two days. Compound U_7O_{20} was prepd. by conversion of uranyl sulfide to oxyacid. Material is black.

306. ON THE LOW OXIDE OF MOLYBDENUM, W. Muthmann. Ann. **238**, 108 (1887).

A comparison of Mo and U oxides is made.

307. ACTION OF NITRIC OXIDE ON METALLIC AND ON METAL OXIDES. P. Sabatier and J. B. Senderens. Compt. rend., **114**, 1476 (1892).

Nitric oxide will not reduce uranium oxide greatly.

308. PEROXIDE, P. Melikoff and L. Pissarjewsky. Z. anorg. Chem. **18**, 59 (1898).

Large number of peroxides, including UO_4 and double peroxides of U with Ba, Na, and Li are mentioned. Peroxides of U and Mo are compared and structures for UO_3 and UO_4 proposed.

309. RECHERCHES SUR L'URANIUM ET SES COMPOSES, J. Aloy. Dissertation, Univ. of Toulouse, (1901). [In Toulouse, Faculte des Sciences de l'Universite, 3 (2) 23 (1901).]

Outstanding dissertation on U prior to recent interest in atomic energy. Literature review (brief bibliography) and original research on the prepn. of U, uranous salts, uranic compounds, and calculations on the at. wt. of U are included. Compounds discussed include oxides, chlorides, bromides, arsenates, oxalates, phosphates, iodides, cyanides, hydroxides, carbonates, etc. Information included is also published by author in short form in various technical journals.

310. THE STATE OF SOME PERACIDS AND THEIR SALTS IN SOLUTION, L. Pissarjewsky. Z. physik. Chem. **43**, 160 (1903).

Disagrees with Fairley [J. Chem. Soc. **31** 125 (1877)] on structure of UO_4. Regards material as free peruranic acid when hydrated with 2 moles of water.

311. THE LUMINESCENCE OF CERTAIN OXIDES SUBLIMED IN THE ELECTRIC ARC, E. L. Nichols and D. T. Wilber. Phys. Rev. **17** (2) 707 (1921).

Thin layers of U oxide when sublimed in an electric arc show no luminescence of high temp. either when excited with flame or when bombarded with cathode rays.

312. ON A NATURAL PERIODIC SYSTEM FOR NONIONIC COMPOUNDS, J. N. Frers. Z. anorg. allgem. Chem. **186**, 145 (1930).

Double uranium compounds (with alk. metals) are considered in so-called 93, 94, 95 groups. Compounds are uranium halides, uranyl halides, and uranium oxides.

313. INTERNATIONALE TABELLEN ZUR BESTIMMUNG VON KRISTALLSTRUKTUREN, (revised edition), 1944. Vol. II.

Contains crystallographic data on many uranium compounds.

314. UNUSUAL COLORS PRODUCED BY URANIUM IN GLASSES, W. Colbert and N. J. Kreidl. J. Optical Soc. Am. **35**, 731 (1945).

When U is introduced into ordinary soda-lime silicate glasses under oxidizing conditions familiar fluorescent yellowish glass is obtained. However, nonfluorescent glasses of various colors (yellow, red, brown, and green) can be obtained by introducing U into other types of glass, either under oxidizing or under strongly reducing conditions. Spectral transmission curves of

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such glasses (including a red which is insensitive to temperature) are given.

315. THE CHEMISTRY OF URANIUM COMPOUNDS, CHAPTER I, A. L. Dounce and J. F. Flagg. MDDC-422, July 1, 1946, declassified Oct. 10, 1946.

Prepn. and properties of some U compounds important in toxicological work are given, including UO_3, UO_4, and U_3O_8. See also: "Pharmacology and Toxicology of Uranium Compounds," Voegtlin and Hodge, McGraw-Hill Book Co., New York, 1949, Chapter 1.

316. SPECTROSCOPIC AND PHOTOCHEMICAL PROPERTIES OF URANIUM COMPOUNDS, WITH PARTICULAR REFERENCE TO ISOTOPIC SEPERATION, G. H. Dieke and A. B. F. Duncan. MDDC-688, declassified Feb. 14, 1947.

Divided into two parts, first titled as above, and second titled "Preparation of uranium compounds." General discussion and literature history is given with bibliography, indexes, and appendixes on absorption and fluorescence wavelengths, special preperations. Preparation and investigations of absorption spectrum (a), fluorescent spectrum (f), temperature effect (t), and isotopic substitution effect (i) on a great number of hydrated UO_2 and UO_4 compounds of nitrates, sulfates, halides, and some selenides. Bondstrengths, lengths, and crystal structure for U and uranyl compounds are also discussed.

317. THE STRUCTURE OF THE CARBIDES, NITRIDES, AND OXIDES OF URANIUM, R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald. J. Am. Chem. Soc. **70**, 99 (1948).

Systems U-C, U-N, and U-O are summarized giving pertinent structural information and necessary details concerning methods used in investigation. **U—C:** UC is face-centered cubic, $a = 4.951$, and has NaCl-type structure. UC_2 is body-centered tetragonal, $a = 3.517$ and $c = 5.987$, and has CaC_2 structure. C is soluble in UC_2 at high temperatures. UC_2 decomposes into UC and C at intermediate temperatures. U_2C_3 probably exists at temperatures above 2000°C., but not at room temperature. **U—N:** UN is face-centered cubic, $a = 4.880$, and has NaCl structure. U_2N_3 is body-centered cubic, $a = 10.678$, and has Mn_2O_3 structure. Sesquinitride structure gradually changes toward ideal dinitride structure in one-phase region extending to composition $UN_{1.75}$. High pressure is needed to form UN_2, which is face-centered cubic, $a = 5.31$, and

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has CaF_2 structure. **U—O:** UO is face-centered cubic, a = 4.92, and has NaCl structure. Very difficult to prepare free from C or N. UO_2 has CaF_2 structure, a = 5.4581. O is soluble in CaF_2 structure to approximately composition $UO_{2.25}$ at which point lattice constant is a = 5.4297. U_2O_5 is orthorhombic, a = 6.72, b = 31.8, c = 8.27. Structure is related to U_3O_8 and UO_3. One phase region exists from U_2O_5 to UO_3 in which various structures continuously transform from one to another. Note: All lattice constants are given in kX units.

318. PURIFICATION OF URANIUM OXIDE, J. I. Hoffman. MDDC-777, declassified March 18, 1947.

Procedure is given for purification of U oxide by converting to nitrate and partitioning nitrate between large amount of Et_2O and relatively small amount of H_2O. In modified form, procedure was found to be applicable to pitchblende, carnotite, and concentrates.

319. INVESTIGATIONS OF OXIDES OF URANIUM. BR-50, declassified April 1947.

Brief note on (1) analysis of residues from black U oxide remaining after treatment with HNO_3, (2) suspensions of oxides in aqueous soln., and (3) preparation of U_3O_8.

320. X-RAY STUDY OF THE URANIUM-OXYGEN SYSTEM, R. E. Rundle, N. C. Baenziger, and A. S. Wilson. MDDC-1273, declassified July 3, 1947.

U-O system studied as function of composition by x-ray diffraction. Several new oxides and transition phases revealed, and structures of oxides determined fully or in part. Phases of U-O system are: (1) between U and UO, two phases, metal phase and cubic monoxide with NaCl structure; (2) between UO and UO_2, monoxide and dioxide, with little solid-solution; (3) between UO_2 and $UO_{2.2}$ or $UO_{2.3}$, one phase with CaF_2 structure, UO_2' spacing decreases as O content of phase is increased. Phase with excess O corresponds to UO_2 from which some U has been removed at random from structure; (4) between $UO_{2.3}$ and U_2O_5, two phases, one is $UO_{2.2}$ with disordered fluorite structure, other is U_2O_5, orthorhombic, closely related to U_3O_8 in structure; (5) between U_2O_5 and U_3O_8, one phase, structure changing continuously with composition; and (6) above U_3O_8, only individual oxides examined, but structure of UO_3 very similar to that of U_3O_8. Evidence that single phases of intermediate character can be produced.

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Structure of UO, UO_2, U_2O_5, and U_3O_8 are described. Summarizes material reported on U oxides presented in earlier reports.

321. THE SPECTRAL ANALYSIS OF URANIUM OXIDE, R. Breckpot. Congr. avance. method. anal. spectrograph produits met. (Paris) 8, 33 (1947).

Systematic study to determine most favorable conditions for preferential excitation of impurity lines of U and other refractory elements. Part of method of fractional sublimation used by Scribner used but with new entrainment agents.

322. THE THERMODYNAMIC PROPERTIES OF EQUILIBRIA AT HIGH TEMPERATURES OF URANIUM HALIDES, OXIDES, NITRIDES, AND CARBIDES, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren. MDDC-1242, declassified Dec. 30, 1947.

Table I contains melting, vapor pressure, and boiling data. Table II gives vaporization equations and constants. Table III gives thermodynamic data for aq. ions which were used in conjunction with data for solid substances. Table IV contains heats of formation and values of $(\Delta F-\Delta H_{298})/T$ from 298° to 1500°K. Table V contains entropies at 298°K and $-(F-H_{298})/T$ for compounds. Table VI gives heat content and entropy increases above 298°K. 123 references are given for data cited and discussion of chemistry of each compound is included, with references. 12 figures are presented to show species that exist when a halide is heated at constant pressure of 1, 10^{-3}, and 10^{-6} atmospheres. See abst. no's. 323 and 327.

323. THE THERMODYNAMIC PROPERTIES AND EQUILIBRIA AT HIGH TEMPERATURES OF URANIUM HALIDES, OXIDES, NITRIDES, AND CARBIDES. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren. MDDC-1543, Sept. 20, 1945, declassified Dec. 30, 1947.

Revision, including new data, on heats of formation of aqueous ions of report MDDC-1242 (1947). See abst. no's. 322 and 327.

324. THE THERMODYNAMICS OF THE ACTINIDES. L. Brewer. MDDC-1722, December 1947, declassified Feb. 16, 1948. Abstract and is reproduced in its entirety.

The available thermodynamic data for the various oxidation states of thorium, uranium, neptunium, and plutonium have been recently compiled by Brewer, Lofgren, and Gilles in declassified AEC papers. The data have been converted to a form which allows

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direct comparison of the stabilities of the various oxidation states of the actinides. The heats of formation of the higher oxidation states from the trivalent state vary regularly through the actinide series. The heats of formation from the metal show alternations which indicate that the properties of the metals do not vary uniformly. The thermodynamic data are also used to predict which oxidation states of the various halides of Th, U, Np and Pu should be stable and preparable. See also abst. No. 326.

325. SPECTROGRAPHIC DETERMINATION OF TRACE MATERIALS IN URANIUM SALTS AND IN MAGNESIUM, DOLOMITE, AND LIME, G. R. Harrison and R. Kent, III. MDDC-1581, declassified Jan. 12, 1948.

Purpose of study was to make quantitative analyses in many thousands of samples of U metal, U oxides of various types, Mg, lime, and dolomite, for any or all of 40 metallic constituents, including rare earths. Development work involved prepn. of std. samples of suitable form, methods of making these, and of burning samples so that stds. would be comparable with them. Tables are given of wavelengths of spectrum lines used, and of sensitivities attained with each element in various types of samples in which it was determined.

326. THE THERMODYNAMICS OF THE ACTINIDES, L. Brewer. AECD-1899, Feb. 10, 1948, declassified April 15, 1948.

Complete document referred to in abst. no. 324. Paper presented orally before Am. Chem. Soc. in April, 1948.

327. THE THERMODYNAMIC PROPERTIES AND EQUILIBRIA AT HIGH TEMPERATURES OF URANIUM HALIDES, OXIDES, NITRIDES, AND CARBIDES. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren. Phys. Rev. 74, 650 (1948).

Paper is summary of data found in reports MDDC-1242 (1947) and MDDC-1543 (1947). See abst. no's. 322 and 323.

328. A PRECISE VOLUMETRIC METHOD FOR THE DETERMINATION OF URANIUM IN URANIUM OXIDES, W. Simon, I. Asbury, and V. E. Flanders. AECD-2652, Aug. 27, 1948, declassified July 20, 1948.

Volumetric procedure using ceric ammonium sulfate as titrant developed for analysis of U in relatively pure samples of U oxide with precision of 0.05% of U present. Procedure differs from standard only in quality of the equipment and in method of dissolving samples. Techniques for sampling and weighing, soln. of

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oxide in hot concentrated H_2SO_4, reduction of sample in Jones reductor, aeration procedures, titration of sample, reagent blank titration, miscellaneous sources of errors, standardization of ceric ammonium sulfate, indicator preparation, and details of experimental procedure are discussed.

329. A HIGH PRECISION METHOD FOR THE VOLUMETRIC DETERMINATION OF URANIUM, M. S. Richmond and C. J. Rodden. AECD-3316, declassified with deletions Sept. 23, 1948.

Uranium was separated from Cu, Fe, and Ni by electrolysis with a Hg cathode. Tetravalent uranium obtained by reduction in a Jones reductor followed by aeration was assayed by adding slight excess of weighed potassium dichromate which was then titrated potentiometrically with 0.01-N ferrous sulfate. Values for U_3O_8 content of standard sample MS-St determined by direct assay of 14 samples, ranged from 99.91 to 99.96% with a mean of 99.93±0.02%. Samples which were electrolyzed before assay gave similar precision but slightly lower results.

330. MINERALOGY OF URANIUM AND THORIUM BEARING MINERALS, D'Arcy George. RMO-563, Jan. 1949.

Report in two parts: section I, devoted to summary of distribution, chemistry, tests, mode of occurrence, and classification of minerals (based in part upon laboratory investigations and in part upon literature studies and field reports); and, section II, devoted to descriptions of the individual minerals.

331. THE CHEMISTRY OF URANIUM. E. I. Rabinowitch and J. J. Katz. AECD-2667, Chapters 11 through 16, declassified Aug. 12, 1949.

Report is continuation of AECD-2624 (see abst. No. 803). Consists of discussion of: Uranium oxides, sulfides, selenides, and tellurides; phase relationships in the U-O system; physical properties of anhydrous oxides; phase relationships and physical properties in the $U\text{-}O\text{-}H_2O$ systems; oxidation and reduction of U oxides and hydroxides; conversion of other compound to oxides and hydroxides; and conversion of U oxides and hydroxides to other U compounds. Extensive literature references included for each chapter.

332. A GLOSSARY OF URANIUM- AND THORIUM-BEARING MINERALS, J. W. Frondel and M. Fleischer. GS-C-74, Apr. 1950.

Glossary is divided into four groups: (A) minerals containing U and Th as major constituents; (B) minerals containing minor

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amounts of U and Th; (C) minerals that, if investigated by modern analytical methods, might show U or Th content; and (D) minerals that are non-U- and non-Th-bearing, but that have been reported to contain impurities or intergrowths of U, Th, or rare-earth-minerals.

333. THE REACTIONS OF URANIUM OXIDES AND LIQUID NITROGEN TETROXIDE, G. Gibson and J. J. Katz. AECD-2877, declassified June 29, 1950.

Liq. NO_2 reacts with U oxides at 25°C and 1.2 atmospheres to form uranyl nitrates containing varying quantities of NO_2. Anhydrous oxides, such as UO_3 and U_3O_8, react slowly and only partially to yield (the nitrate). UO_3 and UO_4 dihydrates react rapidly and completely, also monohydrate of UO_3. All NO_2-containing uranyl nitrates are sensitive to H_2O and lose NO_2 readily on contact with moist air.

334. URANIUM AS FISSIONABLE MATERIAL IN ATOMIC REACTORS, K. Stokland and H. Chr. Neeb. Forsvarets Forskningsinstitutt Arbok III, 1950-51.

Brief summary of methods described in literature for refining U oxides and producing uranium metal from UO_2 is given. Actual process used for Kjeller pile (first Norwegian reactor) is not discussed.

335. PRODUCTION OF URANIUM PEROXIDE, P. Mohr. U. S. Patent No. 2,551,543, May 1, 1951, assigned to US AEC.

Uranium peroxide is pptd. by simultaneous addition of hydrogen peroxide and water soluble base, such as ammonium hydroxide, to soln. containing uranyl salt in such manner as to maintain a pH of 2.5 to 4.0.

336. URANYL PERURANATE, G. Tridot. Compt. rend., **232**, 1215 (1951).

Yellow ppt. obtained by reaction of H_2O_2 with aqueous $UO_2(NO_3)_2$ has been given formulas $UO_4.3H_2O$, $UO_8(UO_2)_2.6H_2O$, $UO_3.H_2O_2.H_2O$, etc. Experiments using various investigative methods resulted in conclusion that substance is $(UO_2)_2UO_8.9H_2O$ at ordinary temperatures; three H_2O molecules being lost between 90° and 120°C, and additional O_2 and H_2O being lost at an unspecified higher temperature.

2.1 Additional references not abstracted

"Communication on the knowledge of the chemical ratio of uranium to other substances. Second Part: On the combining ability of uranium oxide with acids," F. Bucholz. Neues allgem. J. Chem. 4, 134 (1805).

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"Procedure for obtaining pure uranium oxide," L. R. Lecanu. J. phar. sci. assessories 9, 141 (1823).

"Procedure for obtaining pure uranium oxide," L. R. Lecanu and M. Serbat. Quart. J. Sci. **17**, 139 (1824).

"Procedure for obtaining pure uranium oxide," L. R. Lecanu and M. Serbat. J. Chem. Physik (Schweigger) 44, 35 (1825).

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"On metal reduction using other metals in the wet way," N. W. Fischer. Ann. Physik Chem. (Pogg.) **16**, 124 (1829).

"On the preparation of uranium oxide without the direct use of ammonium carbonate," Quesneville. J. prakt. Chem. **6**, 451 (1829).

"On the preparation of uranium oxide without the direct use of ammonium carbonate," Quesneville. J. pharm. chim. **15**, 494 (1829).

"On the atomic weight of uranium and the composition of its oxides and salts," C. Rammelsberg. Ann., **48**, 234 (1843). See also: J. prakt. Chem., **29**, 235 (1843) and Ber. preuss. Akad. Wiss. 79 (1843).

"On the atomic weight of uranium and the composition of its oxides and salts," C. Rammelsberg. J. pharm. chim. 8, 479, (1845). See also: Ann. Physik Chem. (Pogg.), **66**, 91 (1845).

"Purification of uranium oxide from nickel, cobalt and zinc," F. Wehler. Ann. 56, 127 (1845).

"Researches on atomic volume and specific gravity. Ser. 2. On the relation of volumes between simple bodies, their oxides and sulphurets, and on differences exhibited by polymorphous and allotropic substances," L. Playfair and J. P. Joule, Mem. Proc. Chem. Soc. **3**, 57 (1848).

"On the compounds of uranium sesquioxide with acids," A. Girard. Ann. **81**, 366 (1852).

"On the properties of some uranium salts," R. Arendt and W. Knop. Chem. Centr. **28**, 162 (1857).

"Procedure for the preparation and analysis of uranium oxide," L. Kessler. J. pharm. chim. **31**, 182 (1857).

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"On the oxides of manganese and uranium," C. F. Rammelsberg. Sitzber. preuss. Akad. Wiss. 97 (1885).

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"Catalytic oxidation of some aromatic compounds," Y. S. Kal'kind and V. V. Desarev. Zhur. Obshchei Khim. **7**, 879 (1937).

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"Determination of oxygen in uranium by vacuum fusion," L. Brewer. MDDC-366, declassified Sept. 26, 1946.

"The reaction of uranium oxides with sulfur monochlorides," L. Brewer. AECD-2307, July 31, 1948, declassified Sept. 21, 1948.

"Chemical and spectrochemical analysis of uranium and plutonium materials," H. E. Boaz and others. MDDC-279, LADC-170, declassified Sept. 10, 1946.

"Vapor phase chlorination of uranium oxides," H. A. Young and H. G. Reiber. MDDC-1729, Dec. 1947, declassified Feb. 16, 1948.

"A method of making thin uranium oxide films on platinum foils," T. Jorgensen. MDDC-467, LADC-209, declassified Oct. 28, 1948.

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"Analytical chemistry of the Manhattan Project," C. J. Rodden. McGraw Hill, New York, 1950.

3. UO_2 (400-469)

400\. COMMUNICATION ON THE KNOWLEDGE OF THE CHEMICAL RATIO OF URANIUM TO OTHER SUBSTANCES. FIRST PART: ON URANIUM IN REGULINE AND CALCINED STATES, F. Bucholz. Neues allgem. J. Chem. **4**, 17 (1805).

Hydrated uranium nitrate prepd. by the soln. of U oxides in HNO_3. When soln. is evapd., crystals will be deposited and can be recrystd. from water. Data on solubility of $UO_2(NO_3)_2$ in water and FtOH are reported. Prepn. of UO_2 by reduction of higher U oxides is discussed.

401\. CONTRIBUTION TOWARD A CLOSER KNOWLEDGE OF URANIUM, J. A. Arfvedson. Ann. Physik Chem. (Pogg.) **1**, 245 (1824).

Reduction of higher oxides of uranium to UO_2 using hydrogen as opposed to earlier method which used carbon. Crystals are ordinarily micro. octahedra; however, form will vary considerably with method of preparation. UO_2 can also be obtained by reduction of KUO_2Cl_3 with dry hydrogen as long as HCl is evolved. Residue is leached with water and dried. UO_2 obtained is stable in air, goes to U_3O_8 when heated (with swelling) and is insol. in HCl and H_2SO_4. Study of atomic weight of uranium is reported. $BaO.2UO_3$ obtained by pptn. from boiling soln. of UO_2Cl_2 to which $BaCl_2$ has been added while NH_3 is passed through soln. Filtered ppt., which should be washed quickly with boiling water to prevent $BaCO_3$ contamination, is a relatively pure product. $PbO.2UO_3$ prepared from solutions of $UO_2(NO_3)_2$ and $Pb(NO_3)_2$ by pptn. with NH_3. Conclusion is reached that uranyl nitrate is not completely decomposed until entire mass has been converted to U_3O_8.

402\. CONTRIBUTIONS TOWARD THE HISTORY OF URANIUM, L. R. Lecanu. J. pharm. sci. accessories **11**, 279 (1825).

Discussion of reduction of higher oxides of U to UO_2 using H_2 as opposed to C.

403\. RELATIVE STUDIES ON THE ACTION OF WATER VAPOR AT HIGH TEMPERATURE ON METALS AND METALLIC SULFIDES. TRIAL OF A NEW CLASSIFICATION OF METALS ACCORDING TO THEIR DEGREE OF OXIDIZABILITY. V. Regnault. Ann. chim. phys. **62**, 337 (1836).

Water vapor will oxidize UO_2, U_3O_8 is formed.

404. RESEARCH ON THE SPECIFIC HEAT OF ELEMENTS AND COMPOUNDS. FIRST MEMORANDUM: ELEMENTS, V. Regnault. Ann. chim. phys. **73**, 5 (1840).

Average specific heat for uranium (UO_2) for 10° to 98°C was 0.06190.

405. THE PREPARATION OF URANIUM, F. Wohler. Ann. **41**, 345 (1842).

When soln. of $(NH_4)_2UO_4$ in HCl is treated with excess ammonium chloride, evapd. to dryness and fused, leaching of melt with water will leave a residue of black crystalline UO_2.

406. RESEARCH ON URANIUM, E. Peligot. Ann. **43**, 255 (1842); see also Ann. chim. phys. **5**, 5 (1842).

When uranyl oxalate is ignited in dry H_2, followed by cooling in H_2, UO_2 is obtained in pure form, colors are attributed to differences in size of aggregates. Cryst. shape is dependent upon prepn. method; scales with metallic luster were obtained. Not attacked by dil. HCl and H_2SO_4, even when acids are warm. UO_2 is not attacked by gaseous HCl, even at high temps. It will dissolve in concd. H_2SO_4. When uranyl salts are ignited with volatile acids, U_3O_8 formed is usually accompanied by black U_2O_5.

407. RESEARCH ON SEVERAL COMPOUNDS OF URANIUM. J. J. Ebelmen. Ann. **43**, 286 (1842).

Reaction product obtained in prepn. of UO_2 by igniting uranyl oxalate in dry H_2 is first black and then cinnamon-brown. Pryophoric and oxidizes rapidly when heated in air. Density = 10.15. Very pure UO_2 in cryst. form obtained by using five parts Na_2UO_4 with 20 parts of anhyd. $MgCl_2$ in covered crucible. Brilliant black cubes are obtained, easily isolated because of great dens. and stability in presence of dil. acid. When mixed $U^{+4,+6}$ hydroxide is dried in vacuum, black mass obtained. Material exhibits cryst. fracture. If material is rubbed, residue is green powder which maintains const. wt. upon heating in air. Den. of U_3O_8 = 7.31. Brick-red product obtained by dehydration of $UO_3.H_2O$ at 300°C identified as U_2O_7 which goes to U_3O_8 at red heat. Question is raised re actual existence of U_2O_5 proposed by other investigators. Paper contains discussion of solubility of U_3O_8 in acids.

408. UBER DIE VERBINDUNGEN EINIGER MERALLE MIT STICKSTOFF. E. Uhrlaub. Dissertation, Univ. of Gottingen, 1859.

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Method described by Wohler for preparing UO_2 using NH_4Cl and NH_4UO_4 yields an oxynitride of U rather than UO_2. Expts. on the method fail to confirm results.

409. CONCERNING SEVERAL URANIUM COMPOUNDS, H. Hermann. Dissertation, Univ. of Gottingen, 1861.

UO_3 reacts with gaseous mixt. of CO_2 and CS_2 at red heat and will form UO_2. Very pure UO_2, in cryst. form, obtained by heating five parts of Na_2UO_4 with 20 parts of anhyd. $MgCl_2$ in a covered crucible. Brilliant black cubes obtained easily isolated because of great density and stability in presence of dil. acid. UO_2 obtained by ignition of U_3O_8 or Na_2UO_4 with S or NH_4Cl followed by water leaching.

410. ON THE FLUORINE COMPOUNDS OF URANIUM, A. Ditte. Compt. rend. **91**, 115 (1880).

UO_2 obtained by igniting U_3O_8 which has been moistened with a few drops of HF. Particularly simple method of preparing black crystalline UO_2.

411. ACTION OF MOLYBDENUM DIOXIDE UPON SILVER SALTS, E. F. Smith and O. L. Shinn. J. Am. Chem. Soc. **16**, 569 (1894).

UO_2 prepd. by reduction of oxalate is reported to dissolve in an ammoniacal soln. of $AgNO_3$, with the pptn. of metallic Ag.

412. ACTION OF NITRIC OXIDE ON METALS AND METALLIC OXIDES, P. Sabatier and J. B. Senderens. Bull. soc. chim. France **13**, 870 (1895).

Brown UO_2 obtained by reducing UO_3 with H_2 at red heat. Not attacked by N_2O at 150°C, whereas black UO_2 prepd. at a lower reduction temperature is slowly oxidized by N_2O to U_2O_5.

413. RESEARCH ON THE OXIDES OF NITROGEN, NITRIC OXIDE, NITROUS OXIDE, AND NITROGEN PEROXIDE, P. Sabatier and J. B. Senderens. Ann. chim. phys. **7**, 348 (1896).

NO will react with brown UO_2 below red heat, with evolution of light and formation of black U_2O_5. Brown UO_2 obtained by reducing UO_3 with H_2 at red heat. Not attacked by N_2O at 150°C, whereas black UO_2 prepared at a lower reduction temp. is slowly oxidized by N_2O to U_2O_5.

414. SOME OBSERVATIONS ON URANIUM OXIDE, F. W. Oechsner de Coninck. Compt. rend. **135**, 900 (1902).

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When UO_2Br_2 is calcined in air, Br is split off and brick red UO_2 remains. In contrast to product obtained from UO_2Cl_2, UO_2 obtained is oxidized to green U_3O_8. When material is heated in stream of hydrogen, brick-red UO_2 goes to black modification. Use of calcining method for U detn. is described.

415. THE REDUCTION OF REFRACTORY OXIDES BY CARBON, H. C. Greenwood. J. Chem. Soc. **93**, 1483 (1908).

Thermal decomposition of UO_2 begins in vacuum at about 1600°C. When mixture of UO_2 and C is heated electrically in vacuum, reduction begins at about 1490°C where increase in pressure due to evolution of CO occurs.

416. URANIUM COMPOUNDS, F. W. Oechsner de Coninck. Bull. classe sci. Acad. roy. Belg. 992, (1908).

UO_2 obtained by reduction with H_2 at low red heat of orange-red $UO_3.H_2O$. Dark brown UO_2 obtained was converted slowly by H_2O_2 into the hydrate $UO_2.H_2O$, which oxidized to $UO_3.H_2O$ and small amount of green dihydrate. If UO_2 was heated with H_2O_2 almost to the b.p., oxidation was completed more rapidly. With very dil. HNO_3, UO_2 was hydrolyzed; if heated gently it dissolved without oxidizing. By heating to 105° to 110°C, $UO_2SO_4.3H_2O$ lost $2H_2O$; heated higher, some H_2SO_4. If dry salt is heated to low redness it decomps. into UO_3 and SO_3; at red heat it becomes UO_2, SO_3, and O_2; UO_2 oxidized to green U_3O_8. Strongly heated with H_2, black UO_2 was set free from UO_2SO_4. If heated, uranous was converted at low redness to uranic salt; further UO_2 was formed, which was converted to U_3O_8, then U_4O_{10}. U acetate, by dry distillation, gave CO_2 acetone, H_2O, and HOAc besides black (including brown) UO_2, which, heated in air, oxidized. If acetate is heated in air, true black UO_2 was formed.

417. ACTION OF METALLIC OXIDES ON PRIMARY ALCOHOLS, P. Sabatier and A. Mailhe. Ann. chim. phys. **20**, 289 (1910).

Actions of UO_2 and UO_3 are discussed along with other metal oxides. Trials of UO_3 on ethyl, methyl, and benzyl alcohol are described. UO_2 is reported to act as catalyst in formation of primary alcohol.

418. A DETERMINATION OF THE MOLECULAR WEIGHT OF URANIUM OXIDE, F. W. Oechsner de Coninck. Compt. rend. **152**, 711 (1911).

418—Continued

Mol. wt. of UO_2 determined by reduced UO_2Cl_2 with H_2 according to the equation: $UO_2Cl_2 + H_2 \rightarrow 2HCl + UO_2$. Five determinations gave mean value of 270.07.

419. DETERMINATION OF THE MOLECULAR WEIGHT OF URANOUS OXIDE, F. W. Oechsner de Coninck. Compt. rend. **152,** 1179 (1911).

Pure $UO_3.H_2O$ was reduced with H_2 at bright-red heat. Using 238.5 as at. wt. of U and 304.5 as mol. wt. of $UO_3.H_2O$, means of 5 detns. gave 270.66 as mol. wt. of UO_2, the theoretical value being 270.5.

420. SOLUBILITY OF URANOUS OXIDE IN SEVERAL ACIDS, A. Raynaud. Compt. rend. **153,** 1480 (1911).

Soly. by wt. in HCl, HBr, H_2SO_4, HNO_3, HOAc, and aqua regia are reported to be UO_2: acid, 1:3100; 1:4650; 1:2200 (66°Be.); 1:8 (36°Be.); 1:12,000; and 1:29.6. All values are at temps. near 18°C. UO_2 was obtained by calcining $UO_2C_2O_4$, which had been purified by several crystns., in a closed crucible.

421. A NEW URANIUM COLLOID, A. Samsonow. Z. Chem. Ind. Kolloide **8,** 96 (1911).

By electrolysis of soln. of UO_2Cl_2 a black ppt. forms, sol. in H_2O and shows Brownian motion when freshly dissolved. Colloid is attracted to neg. pole of battery and is pptd. by neutral electrolytes though not by acids. Analysis shows it to consist entirely of UO_2. Reduction of UO_2Cl_2 by Zn or Cu in dil. HCl soln. gives same colloidal soln; reduction of sulfate fails, propably because of soly. of colloid in H_2SO_4.

422. THE ACTION OF ACIDS ON URANOUS OXIDES, A. Colani. Compt. rend. **155,** 1249 (1912).

UO_2 was obtained by heating pure green oxide in a current of H_2, also, by heating $UO_2C_2O_4$ in a current of H_2 at a lower temp. Obtained by latter method, found to be more sol. in HCl than by former. Both forms are slightly soluble in HCl if allowed to react a long time (2 to 28 weeks). Results reported by Raynaud are low because time of solution was too short.

423. URANYL OXALATE, F. W. Oechsner de Coninck and A. Raynaud. Bull. soc. chim. France **11,** 531 (1912).

$UO_2C_2O_4$, recrystd. several times, contains 3 moles H_2O. Sol. in H_2O but slightly sol. in EtOH or MeOH. H_2O escapes when salt

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is heated to 100° for 4 hours. Upon calcination, pure UO_2 is left in form of black powder, not readily sol. in hydroacids or in H_2SO_4, but readily sol. in HNO_3 or aqua regia. Dry oxalate absorbs water from air, incompletely unless air is moist. Calcination of salt must be done carefully, with exclusion of air; otherwise, pyrophoric UO_2 is formed and, consequently, UO_3.

424. ON THE DENSITY OF URANOUS OXIDE AND ITS SOLUBILITY IN NITRIC ACID AND IN AQUA REGIA, A. Raynaud. Bull. soc. chim. France **11**, 802 (1912).

Graph showing sol. of UO_2. Density of UO_2 is 8.2.

425. ON THE ELECTRIFICATION ASSOCIATED WITH DUST-CLOUDS, W. A. D. Rudge. Phil. Mag. **25**, 475 (1913).

Finely divided UO_2 or UO_3 when dispersed in strong blast of air, will acquire positive charge of static electricity. Many other materials were also investigated.

426. PREPARATION OF BLACK OXIDE OF URANIUM (UO_2), C. L. Parsons. J. Ind. Eng. Chem. **9**, 466 (1917).

UO_2 may be prepd. by fusing $Na_2U_2O_7$ with NaCl and charcoal. Permits recovery of vanadic acid which may be contd. in Na_2UO_4 as an impurity.

427. STUDY OF THE REVERSIBLE REACTIONS OF HYDROGEN AND OF CARBON OXIDE ON THE METALLIC OXIDES, G. Chaudron. Ann. chim. **16**, 221 (1921).

Pgs. 251-2 contain information on attempts made to confirm early work of Regnault (1836) on oxidation of UO_2 by H_2O vapor. Expts. reported by early experimenter showing U_3O_8 could not be duplicated.

428. RELATIONS BETWEEN THE DIFFERENT URANIUM OXIDES, P. Jolibois and R. Bossuet. Compt. rend. **174**, 386 (1922).

When UO_2 is heated in O_2, it will oxidize to U_3O_8 within a very narrow temp., beginning at 185°C, without appearance of any intermediate oxide phase. Reduction of damp or dry UO_3 or U_3O_8 in stream of H_2 will yield very pure UO_2. Reduction is carried out at 900° to 1200°C. UO_3 heated in vacuum at 500° begins to go over to U_3O_8, decomposition is not reversible. Reduction of U_3O_8 in H_2 atm. at 625° to 650°C was found to be successful. It is quantitative if H_2O produced is continually removed by P_2O_5. No other reaction takes place as high as 1000°C. If U_3O_8 is heated in vacuum for about 3 hours at 1000°C, it will lose oxygen to composition of about $UO_{2.62}$. To prep. nitrate-free UO_3, decompn. must be carried out at about 500°C.

429. ON THE OXIDES OF URANIUM, P. Lebeau. Compt. rend. **174,** 388 (1922).

Powdered gray product is obtained, which will not lose weight at 1000°C, when U_3O_8 is heated to 800°C. Discussion of reduction of damp or dry UO_3 or U_3O_8 in stream of H_2 which yields very pure UO_2. Reduction is carried out at 900° to 1200°C. UO_2 product is chestnut-brown and reduction was found to begin at about 500°C. Examination of method of heating U_3O_8 with a few drops of HF in order to prepare UO_2; however, method does not prevent reoxidation to U_3O_8 in O_2. Regardless of prepn. method, true UO_2 is brown. UO_3 shows no noticeable change when heated in air to 600°C; decomposition is evident at 700°, and is rapid and complete at 800°. U_3O_8 prepd. below red heat will never be completely pure, always containing some UO_3. UO_3 in moist air, at ordinary temps., was found to go to $UO_3.2H_2O$. U_3O_8, prepd. by heating uranyl oxalate in covered crucible at 350°, is grayish-black. If product is heated for 12 hours in air at 350°, it turns orange-brown and shows almost exactly increase in wt. which would be required to convert it to UO_3.

430. CRYSTAL STRUCTURE OF NATURAL AND OF SYNTHETIC OXIDES OF URANIUM, THORIUM, AND CERIUM, V. M. Goldschmidt and L. Thomassen. Videnskapsselskapets-Skrifter. I. Mat.-naturv. Klasse, Kristiania, No. 2, (1923).

Minerals pitchblende, broggerite, cleveite, and thorianite, and pure oxides UO_2, UO_3, U_3O_8, ThO_2 and CeO_2 were studied. Debye-Scherrer diagrams were made by means of rays from Hadding-Siegbahn metallic Roentgen tube with Al windows, source of rays being an Fe anticathode. Apparatus, methods of work and of calculation are described in detail. Results are shown in 18 tables. Detailed descriptions are given of minerals and of methods used in preparing oxides. UO_2, ThO_2 and CeO_2 are isomorphous, metallic atoms being arranged in face-centered cubic lattices. Three different geometrical possibilities exist for arrangement of O atoms, most probable being that of fluorite type. Crystal structure of U_3O_8 is essentially different from that of UO_2, and crystals do not belong to isometric system. UO_3 was obtained only in amorphous state. Cleveite, broggerite, and thorianite have definite crystalline structure, with atomic arrangement corresponding to original crystal lattice. Structure of these minerals corresponds to that of isomorphous mixtures of UO_2, ThO_2, some CeO_2, and eventually to dioxide of U-Pb. Therefore, broggerite and other varieties of uraninite do not belong to spinel group. Lattice dimensions (kX units) were thorianite = 5.57, broggerite = 5.47, cleveite = 5.47, and UO_2 = 5.47. Cleveite, which is rich in UO_3, is transformed to U_3O_8 by heating to 800°C. Broggerite, after heating, has structure of UO_2. Pitchblende from Joachimsthal contains crystalline material of isometric system in strongly dispersed condition. U atoms are arranged in face-centered cubes with edges 5.42 to 5.45 x 10^8cm, therefore, smaller than those of pure UO_2, perhaps in consequence of isomorphic replacement of U by an atom of smaller vol. Probably taking up of an excess of O_2 in crystallization of UO_2 is in its geometrical relation comparable to taking up of an excess of F atoms in yttrofluorite. It is noteworthy that minerals so strongly radioactive and so old as broggerite and thorianite can entirely or largely keep their original atomic arrangement, notwithstanding for example broggerite, perhaps one out of 8 uranium atoms transformed into Pb.

431. THE REDUCTION OF SCARCELY REDUCIBLE METAL OXIDE WITH HYDROGEN, H. von Wartenberg, J. Broy, and R. Reinicke. Z. Elektrochem. **29**, 214 (1923).

UO_2 was found to be stable to H_2 even at high pressure (25 atms) and high temps. (m.p. of W).

432. KRISTALBOUW EN PHYSISCHE EIGENSCHAPPEN, A. E. Van Arkel. Physica **4**, 286 (1924).

Unit cell of wolfram (UO_2) is 3.15 A, a is 5.48 kX, used $CuK_{\alpha 1}$ radiation.

433. PREPARATION AND PROPERTIES OF HIGH-MELTING LOWER OXIDES, E. Friederich and L. Sittig. Z. anorg. allgem. Chem. **145**, 127 (1925).

UO_2 (brown in H_2 and blue in N_2) was prepd. from U_3O_8. Hardness of about 5 and melts from 2500° to 2600°C. Electrical resistance is very high.

434. THE SIZES OF IONS AND THE STRUCTURE OF IONIC CRYSTALS, L. Pauling. J. Am. Chem. Soc. **49**, 765 (1927).

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Discussion of crystal structure of UO_2. Empirical calculation of radius of U^{+4} ion in crystal lattice yields 0.97A. For UO_2 of fluorite-type structure, the lattice ratio is reported as 0.69.

435. IONIC SIZES AND THEIR RELATIONSHIP TO CRYSTAL STRUCTURE TYPE, SOLID SOLUTION AND DOUBLE SALT FORMATION AND THE STABILITIES OF HYDRATES AND AMMONIATES, E. J. Cuy. J. Am. Chem. Soc. **49**, 201 (1927).

Interatomic distance in UO_2 (2.37 kX) and assumed radius for U^{+4} (1.22 kX) are reported. Structure type (I) and ratio of atomic radii (0.94) are also reported for UO_2.

436. TEMPERATURE AND STABILITY OF COLLOIDAL SOLUTIONS, S. J. Djatschkowshy. Kolliod-Z. **54**, 278 (1931).

Curve of surface tension of 1% UO_2 soln. as function of temp. shows max. at 30° to 40°C. Stability of soln. is examined over range 10° to 70°C.

437. URANIUM DIOXIDE RESISTORS, G. W. Mueller. AEG Mitt. 267 (1934).

W lamp filament and Fe wire in H_2 gave positive temp. coeff. To meet demand for convenient neg. temp. coeff. resistor, UO_2 resistors were developed. Ohmic resistance is practically const. even after many thousand hrs. of service. UO_2 unit is mounted in lamp bulb filled with N_2 or other suitable gas. Units for currents as low as 0.1 amp and as high as 30 amps. are available. Potential range is 115 to 380 v. During operation, UO_2 attains temperature of about 300°C. Resistors are particularly useful when connected in series with any electrical device which ordinarily "overshoots" when circuit is closed. Cold ohmic resistance of UO_2 drops to about 1/50 of its value during 0.5 to 30 sec (depending upon size) after circuit is closed. Slow drop in resistance may be practically utilized in operating a magnetic relay.

438. RESISTANCES, Patent Treuhand Gesellschaft fur elektrische Gluhlampen m. b. H. British Patent No. 409, 174, April 26, 1934.

Electrical resistance with neg. temp. coeff. and for use particularly with Fe-H resistors is prepared from UO_2.

439. NOTE SUR LE RESCAU DE L'URANINITE, A. Schoep and V. Billiet. Ann. soc. geol. Belg. Bull., **58**, 198 (1935).

Lattice is fluorite type with space group O_h^5 - Fm3m and four molecules per unit cell, a = 5.48 A (converted from kX).

440. THE MEASUREMENT OF THE DIELECTRIC CONSTANT IN THE CENTIMETER BAND, A. N. Sus. Doklady Akad. Naul S.S.S.R. **33**, 310 (1941).

By use of free-wave method of Velasco and Hutchinson [Proc. Phys. Soc. **51**, 679 (1939)] dielectric constant in the cm band was determined for UO_2 equal to 9.5. Accuracy of measurements varied from 1 to 5%. For thin materials, effect of thickness is linear, so that measurements can be made on a single specimen. Further research was designed to extend method to double layers.

441. NEGATIVE RESISTANCES, W. Amrein. Schweiz. Arch. angew. Wiss. Tech **8**, 85 (1942).

Term "neg. resistance" applied to resistance with neg. coef. characteristic. With its use a completely resistanceless conductor can be realized. Only solid conductors are discussed, or, more correctly, semiconductors whose resistance varies with temp. (so-called "hot conductors") and which show a neg. characteristic above a certain c.d. Experiments described to attain limiting freq. of 2000 to 3000 cps. Non-reversible characteristics and low limiting freqs. were obtained with sintered UO_2 (density = 9.2, sp. heat = 0.26 w sec/°, thermal cond. = 0.062 w/cm/°, Mohs hardness = 6 to 7) which had been pressed into small rods in vacuum. Thin fibers (0.2 mm in diam.) and long, thin splinters of sintered oxide rods on which a porcelain glaze was fused were also used. (Splinters laid on top of glazed electrical porcelain and heated until splinters were imbedded in molten glaze.) Effect of neg. resistance developed is shown with aid of characteristic curves.

442. PREPARATION AND PROPERTIES OF SULFIDES AND OXIDE-SULFIDES OF URANIUM, E. D. Eastman, L. Brewer, L. A. Bromley, P. R. Giles, and N. L. Lofgren. MDDC-193, July 24, 1945, declassified Aug. 17, 1946.

Methods for prepn. of US, U_2S_3, and US_2 are reported. US_2 and intermediates of U_2S_3 are prepd. by H_2S treatment of UO_2 or U_3O_8 in C system at 1200° to 1300°C. In this method UOS is an intermediate and C of system enters reaction in its conversion to pure sulfides.

443. ELECTRICAL RESISTANCE OF THE CONTACT BETWEEN A SEMICONDUCTOR AND A METAL, A. V. Ioffe. Fiz. Zhur. **10**, 49 (1946).

Contact resistance and potential of semiconductor and metal were investigated with currents in both directions. For semiconductor UO_2 it was found that, close to metal, there arises

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considerable additional resistance when an electron semiconductor borders on a metal possessing a higher contact potential or when a hole semiconductor borders on a metal having a lower contact potential. Contact potentials were found to be independent of temperature and of specific conductivity. Conductivity was estimated and its dependence on the p.d., temperature, and current direction was studied. Feeble rectification observed.

444. HIGH-TEMPERATURE HEAT CONTENTS OF URANIUM, URANIUM OXIDE, AND URANIUM TRIOXIDE, G. E. Moore and K. K. Kelley. J. Am. Chem. Soc. **69**, 2105 (1947).

High-temperature heat contents of U, UO_2, and UO_3 were measured from 298.16° to 1300°, 1500°, and 900°K, respectively, by methods previously described by Southard (see original document). Metal was found to exhibit two sharp transitions: at 935° and at 1045°K. Results near these temps. were accurately reproducible and there was no evidence of hysteresis. Equations representing heat-content results, range of validity, and mean derivation are:

$$\text{for } UO_2,\ H_T - H_{298.16} = 19.20T + 0.81 \times 10^{-3} T_2 + 3.957 \times 10^5 T^{-1} - 7124 (298\text{-}1500°K)\ 0.1\%$$

$$\text{for } UO_3,\ H_T - H_{298.16} = 22.09T + 1.27 \times 10^{-3} T_2 + 2.973 \times 10^5 T^{-1} - 7696 (298\text{-}900°K)\ 0.1\%$$

These yielded following equations for heat content:

$$UO_2,\ C_p = 19.20 + 1.62 \times 10^{-3} T - 3.957 \times 10^5 T^{--}$$

$$UO_3,\ C_p = 22.09 + 2.54 \times 10^{-3} T - 2.973 \times 10^5 T^{--}$$

Table of heat contents and entropy increaments above 298.16°K compiled.

445. A COMPARISON OF THE GRAVIMETRIC AND VOLUMETRIC DETERMINATIONS OF FREE UO_2 IN URANIUM DIOXIDE, S. H. Anonsen, R. W. Bragdon, C. L. French, and G. L. Martin. MDDC-1435, June 1947, declassified Nov. 6, 1947.

Ignition assay of brown oxide for free UO_2 is subject to error due to tendency of powdered material to adsorb H_2O. Method is recommended for use only where speed is more important than accuracy. Volumetric method of assay is recommended for accurate determinations.

446. ENTROPY, SPECIFIC HEAT, ETC., DATA ON U, UO_2, AND UO_3. MDDC-1499, Dec. 24, 1942, declassified Dec. 10, 1947.

Consists of tables giving heat contents of U, UO_2 and UO_3 above 298.16°K (400° to 1500°K) as obtained from smooth curves and from experimental results.

447. OXIDATION OF URANIUM DIOXIDE (UO_2), F. Gronvold and H. Haraldsen. Nature **162**, 69 (1948).

UO_2 (a = 5.468A, converted from kX) was heated in oxygen from 100° to 265°C, and products examined by x-ray powder method. At 150° UO_2 takes up oxygen to $UO_{2.34}$. Change to lower symmetry is indicated (a = 5.40 kX). Change from UO_2 to $UO_{2.34}$ is accompanied by an increase in density from 10.80 g/cc. In the range 200° to 250°C, oxygen exceeds $UO_{2.34}$ and a new phase, beta, is formed. Phase is tetragonal with constants, a = 5.37, c = 5.54 (kX units) and c/a = 1.03. Calculated densities given are $UO_{2.34} = 11.46$; $U_{0.88}O_{2.12} = 10.04$; $U_{0.82}O_2 = 9.44$. U atoms form face-centered lattice (0,0,0; 0; ½,½,0,½; ½,0,½,½). Observed and calculated intensities are in good accord. Phase near composition U_2O_5 was found, stable below 260° to 270°, as a tetragonal deformed UO_2 with composition not to exceed $U_{0.88}O_{2.12}$. U_3O_8 has homogeneity between $UO_{2.67}$ and $UO_{2.56}$.

448. DETERMINATION OF THE SURFACE AREA OF URANIUM COMPOUNDS OF DIFFERENT PARTICLE SIZES BY LOW-TEMPERATURE VAN DER WAALS ADSORPTION OF ETHANE, K. Lauterback, S. Laskin, and L. Leach. AECD-2244, declassified Aug. 3, 1948.

To extend scope of information of physicochemical properties of U dusts, surface area measurements were made on several representative U compounds. Experimental method most suitable to purpose was found to be low-temperture gas adsorption. Using modified apparatus developed by Wooten and Brown, C_2H_6 (at -183°C) was chosen as adsorbate in order to evaluate very small surface areas encountered. U compounds investigated were UO_2, UO_3, UO_4. With exception of UO_4, all compounds exhibited fairly low specific surfaces of order of from 0.4 to 0.7 m^2/g. Corresponding specific surfaces determined from direct micro. measurements showed a similar range of values. Specific surface determinations were also carried out on two solid samples, which were obtained by drying aqueous suspensions of fine and coarse UO_2 dust. Fine material showed tenfold larger area of 4.23 m^2/g as compared with 0.47 m^2/g for coarse suspension. Corresponding calculated specific surfaces, however,

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showed only a fivefold larger area for fine suspension. Difference and relatively high porosity values of 14.1 for fine suspension and 6.8 for coarse suspension indicate a change in physical structure of material or leaching of surface associated with process of preparing suspension. Results are similar to findings on increased surface areas associated with washing of sized glass beads. See also J. Franklin Inst. **250**, 13 (1950)

449. URANIUM MONOCARBIDE AND METHOD OF PREPARATION, H. A. Wilhelm and A. H. Daane. U. S. Patent No. 2, 448, 479, Aug. 31, 1948, assigned to US AEC.

U carbides of low C content (less than 10%) have structural strength and resistance to wear superior to metallic U or U oxide. Process is shown preparation of carbides (represented by formulas UC, UC_2, and U_2C_3) from oxides UO_2 or U_3O_8 and C, mixed in stoichiometric proportions and heated in crucible below melting point of carbide expected. Several variants of method, which concern mode of mixing, heating, etc., are covered.

450. PREPARATION DE L'OXYDE D'URANIUM UO_2 DE DENSITE ELEVEE (8 A 9), C. Eichner, A. Ertaud, Y. Ortel, J. Stohr, and L. Vautrey. Commissarist a l'Energie Atomique. CEA -35, Oct. 1948.

UO_2 prepared from UO_4 by thermal reduction with H_2 (heated to 350°C and exothermic reaction raised temperature to 900° or 1000°C). High density was obtained by hydraulic compression in 3-piece tubular mold.

451. W. H. Zachariasen lecture at New Haven, Conn., 1948.

Lattice constant of UO_2 is $a = 5.4568 \pm 0.0005$ A.

452. THE OXIDES OF URANIUM. K. B. Alberman and J. S. Anderson. J. Chem. Soc. (London) Suppl. No. 2, S303 (1949).

Phase equilibria in U-O system between composition limits UO_2 and $UO_{2.3}$ investigated in detail with regard both to structure of phases formed and to kinetics of formation from UO_2 and O_2. UO_2, possesses fluorite structure, will take up O at temperatures below 230°C to composition $UO_{2.2}$ without change of structure or appreciable change of cell dimension. Oxides in this composition range disproportionate when annealed at high temperatures into 2 well-defined cubic phases, viz., UO_2 and phase of composition close to $UO_{2.2}$ (beta-UO_2). Oxides in composition range $UO_{2.2}$ to $UO_{2.3}$, prepared below 230°C, have tetragonal structure with axial ratio

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c/a changing progressively with composition; these oxides disproportionate on heating into beta-cubic phase and U_3O_8-like structure. Kinetic studies of oxidation process suggest that oxidation proceeds by way of diffusion-controlled reaction in solid phase of variable composition. Studies suggest general similarity between oxides of U and those of Mo and W.

453. QUANTITATIVE ANALYSIS OF UO_2-U_3O_8 MIXTURES BY X-RAY DIFFRACTION, F. N. Bensey and A. C. Eckert. AECD-2581, Mar. 8, 1949, declassified May 5, 1949.

Method of quantitative analysis using x-ray diffraction applied to determination of UO_2 in UO_2-U_3O_8 mixtures containing 1 to 30% UO_2 by wt. Two techniques employed in analysis: one, pattern is recorded photographically, and, in other, diffracted x-rays are measured by Geiger counter spectrometer. Photographic method is good to lower concentration limit of 2% and Geiger counter spectrometer has a lower limit of 1%.

454. THE PURIFICATION OF URANIUM, B. Goldschmidt. Atomes, **4**, 52 (1949).

Briefly, method used for obtaining uranium compounds pure enough for use in French pile consisted in extraction of $UO_2(NO_3)_2$ with Et_2O, ppt. the $UO_2(NO_3)_2$ as UO_4 with H_2O_2, converting UO_4 to UO_3 with heat, and reducing UO_3 to UO_2 in stream of H_2. By procedure strong neutron absorbers such as B, Cd, Li, and certain rare earths were eliminated.

455. THE MANUFACTURE OF BILLETS OF URANIUM OXIDE, J. A. Stohr. Atomes **4**, 57 (1949).

Billets for French pile and constructed of Al tubes filled with brown UO_2 obtained by reduction of UO_3 in stream of H_2. Density of brown powder is increased (by using press and mold) to approximately 6. Density of compressed pieces further increased by fritting process, which in brief consists in heating to high temperatures (around 1600°C) in H_2 and N_2 atmosphere until specific gravity of approximately 10 is reached.

456. HIGHER OXIDES OF THE ACTINIDE ELEMENTS. THE PREPARATION OF Np_3O_8, J. J. Katz and D. M. Gruen. J. Am. Chem. Soc. **71**, 2106 (1949).

Effort was made to prepare higher Np oxides (with O-Np ratio greater than 2) to compare properties with analogous compounds of other actinide elements: in this case U oxides. NO oxidation of U_3O_8 above 250° resulted in brick-red anyhdrous UO_3 with crystal structure distinct from other known phases of UO_3. NO oxidation of UO_2 resulted in products varying in composition from $UO_{2.2}$ to $UO_{2.9}$, depending upon temperature. Thermal decomposition curves of UO_3 and Np_3O_8 were compared. Former showed region of stability corresponding to formula $UO_{2.91}$.

457. STUDY OF OXIDE OF URANIUM THERMISTORS. J. Prigent. J. Phys. radium **10**, 58 (1949).

Attempts to prepare U oxide thermistors (to detect infrared and ultrahertzian radiations) are described. Methods of preparation of UO_2 are described and data obtained on various properties of pastes of U oxide, i.e., resistance and influence of applied force, temperature and pressure, are given in form of curves. Practical application of samples obtained not very satisfactory and other oxides usually are used.

458. SUMMARY OF RESEARCH ON EXPERIMENTAL REFRACTORY BODIES OF HIGH-MELTING NITRIDES, CARBIDES, AND URANIUM DIOXIDE, P. Chiotti. AECD-3204, ISC-44, Apr. 23, 1949, declassified July 16, 1951.

Procedures for preparation of nitrides of Be, La, Ta, Th, Ti, Zr, and U and monocarbides of Nb, Ta, Ti, Zr, and U and preparation of refractory bodies from them are described. Reasonably strong and dense bodies can be prepared from these as well as from UO_2. Evidence showing tendency toward instability at high temperatures of Be_3N_2, TaN, and ThN is presented. Evidence is given indicating that the hexagonal structure reported by others for TaN is actually that for Ta_2N. Lattice for Th_2N_3 is proposed. Melting points of ThN, UN, and UC are determined to be 2630° ±50°C, 2650° ±100°C, and 2590° ±50°C, respectively.

459. A GENERAL INTERPRETATION OF THE pH-VISCOSITY RELATIONSHIP FOR AMPHOTERIC CERAMIC OXIDE SLIPS, P. Murray. AERE-M/R-507, Apr. 1950.

pH-viscosity and pH-sedimentation volumetric relationships determined for concentrated UO_2 slips and show marked similarity to each other and to pH-viscosity curve obtained by other workers for

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alumina. Shapes of curves for UO_2 are tentatively explained on assumption that U hydroxide possesses amphoteric characteristics and that solid particles of slip can absorb complex metal anions or cations. Calculations based on this hypothesis give pH-neutralization curves which agree with experimental viscosity and sedimentation curves. Analogy has been noted between this phenomena and pH-solubility curve for silver oxide. Satisfactory UO_2 crucibles can be made by slip casting at pH 2.1.

460. Lattice constant and density of UO_2, J. R. Arnott, Am. Mineral. **35**, 386 (1950) quotes Dana's system of mineralogy, Vol. 1, 7th Ed., 1944 (New York).

a = 5.48 kX, density = 10.95.

461. THE HEATS OF COMBUSTION OF THORIUM AND URANIUM, E. J. Huber, Jr., C. E. Holley, Jr., and E. H. Meierkord. AECU-1294 (LADC-960), 1950.

Precise measurements of heats of combustion of Th, U, and U dioxide made and heats of formation of ThO_2, UO_2, and U_3O_8 calculated. Final values for the various materials are: thorium, heat of combustion in 25 atm. oxygen = 5276 ± 7 joules/g.; heat of formation of ThO_2, $\Delta H_{25^\circ C} = -1227.4 \pm 1.5$ kjoules/mole; uranium dioxide, heat of combustion in 25 atm. oxygen = 389.23 ± 0.46 joules/g.; heat of reaction $3UO_2 + O_2 = U_3O_8$, $\Delta H_{25^\circ C} = -318.01 \pm 0.37$ kjoules/mole; uranium, heat of combustion to U_3O_8 in 25 atm. oxygen = 4984.7 ± 9.7 joules/g.; heat of formation of U_3O_8, $\Delta H_{25^\circ C} = -3570.9 \pm 6.9$ kjoules/mole. It was necessary to cut U into small pieces and mix with UO_2 in order to oxidize it completely to U_3O_8. Heat of formation of UO_2 calculated is $\Delta H_{25^\circ C} = -1084.3 \pm 2.5$ kjoules/mole.

462. MINERALOGICAL STUDIES OF URANINITE AND URANINITE-BEARING DEPOSITS; JULY 1, 1949 TO JUNE 30, 1950, P. F. Kerr, RMO-715, July 1, 1950.

Uraninite ore studied in detail. Work by various investigators indicates considerable range of measurements for lattice constants of uraninite. Causes of these variations investigated and discussed. X-ray diffraction patterns of different uraninite specimens and uranium oxides are shown. Structural changes obtained by heating artificial UO_2, UO_3, U_3O_8, and hard lustrous uraninite shown diagrammatically. Differential thermal curves are illustrated

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representing uraninite specimens, thorianite, and oxides UO_2, UO_3, and U_3O_8. Photographic plates show changes in crystallization corresponding to stages in thermal analyses.

463. NOTE ON MEASUREMENT OF THERMAL CONDUCTIVITY OF SINTERED URANIUM DIOXIDE, M. Englander. CEA-79, June 1951.

Thermal conductivity of sintered UO_2 determined by measuring quantity of heat passed in unit time through plate of given dimensions when certain temperature difference was being maintained at faces of plate. Specimens, about 10 to 40 mm thick and about 65 mm in diam., were heated electrically, temperature of both faces measured by iron-constantan thermocouples. Accuracy of device at present is not high, relative error being about 15%. Thermal conductivity of sintered UO_2 in temperature range 20° to 250°C was 9×10^{-3} cgs units.

464. ON URANIUM OXIDES OF VARIABLE COMPOSITION, A. Boulle, R. Jary, and M. Domine-Berges. Compt. rend. **233**, 1281 (1951).

Existence of tetragonal U_3O_7 in homogeneous phase between UO_2 and U_3O_8 is shown by oxidation-reduction and x-ray diffraction experiments. No intermediates, such as U_2O_5, were found between U_3O_7 and U_3O_8. Composition U_3O_7 is difficult to reconcile with concept of definite compound.

465. NBS Rept. 1353, Nov. 1951, to ASTM, H. E. Swanson and R. K. Fuyat.

Three strongest lines for NBS pattern of UO_2 are 111, 220, 200, a = 5.4682A, 26°C. Density calculated from NBS lattice data is 10.968. (To be published as NBS Circular.)

466. PROCESS FOR ELECTRODEPOSITING URANIUM DIOXIDE, M. Kahn. U. S. Patent No. 2,581,863, Jan. 8, 1952, assigned to U. S. AEC.

Patent describes process for preparing thin films of metal compounds, such as uranium oxides and hydroxides, suitable for determination of radioactivity thereof by counting techniques. Thin, uniform film of metal compound is produced by electrodeposition from alkaline soln.

467. DIFFRACTION OF SLOW NEUTRONS BY MICROCRYSTALLINE URANIUM DIOXIDE AND CERIUM DIOXIDE, F. Verdaguer, C. Sanches del Rio, R. Keller, and A. Kind. Helv. Phys. Acta, **25**, 79 (1952).

Measurements of transmission of monokinetic neutrons by microcrystalline UO_2 and CeO_2 powders, and study of resulting curves of cross sections as functions of associated wave length, resulted in determination of value and sign of U and Ce scattering amplitudes.

468. STUDIES OF RADIOACTIVE COMPOUNDS: IV-PITCHBLENDE FROM LAKE ATHABASKA, CANADA, E. J. Brooker and E. W. Nuffield. Am. Mineral. 37, 363 (1952).

Six specimens of pitchblende analyzed for U^4 and U^6 content and x-ray powder photographs obtained before and after heat treatments. Cell edges of pitchblende range continuously from 5.470 to 5.395 A. Decrease is due to oxygen entering interstitial positions in UO_2 structure with consequent change of U^4 to smaller U^6 ion. Lowest cell edge represents composition of near $UO_{2.6}$; solid-solution range of laboratory-prepared cubic oxides ceases at about $UO_{2.2}$ to $_{2.3}$. Oxidation is not uniform throughout a pitchblende specimen and this together with reduction in grain size results in loss of definition in powder pattern. Term "Metamict" is not applicable in this connection. Cell dimensions of U_3O_8 increase as oxygen enters structure. Used pitchblende which applies to material which is formed from hydrothermal solutions. Usually fine-grained, seldom crystallized, and contains only minor amounts of rare earth elements and thorium. Uraninite is characteristically a syngenetic mineral in granitic igneous rocks. Frequently crystallized and contains appreciable amounts of rare earth elements and thorium. Cell edge of uraninite is characteristically longer than that of pitchblende, approaching that of thorianite. Both minerals have ideal composition UO_2 and fluorite-like structure. To reduce problem of the variation in cell dimensions to simple proportions study was made using pitchblende which is relatively free of extraneous elements. Three x-ray powder patterns made for each of six samples, varying in amounts of U^6 from 17.4 to 85.0%: (1) in the natural state, (2) after heating in vacuum for 1/2 hour, (3) after heating in air at about 900°C for 5 minutes. After heating 1/2 hour in vacuum all samples gave pitchblende pattern (which was not found in natural state), further, cell edges were reduced for all specimens were cell edge of untreated material was higher than $a = 5.405A$. None of samples gave UO_2 pattern after heating in air for 5 minutes. Milne [Am. Mineral. **36**, 415 (1951)] noted and confirmed during study: the majority of U_3O_8 powder patterns show double hexagonal cell instead of orthorhombic cell generally associated with U_3O_8. Amorphous UO_3, reported by Zachariasen, was

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actually reduced to single cell type U_3O_8—phase with loss of some oxygen during heating procedure, rather than recrystallized to another form of UO_3. Highly oxidizing conditions apparently favor production of single cell type; Milne reported only one sample of U_3O_8, prepared by heating uranyl nitrate in air at 220°C for several days, resulted in simple structure. In study only those specimens high in U^6 produced single cell type U_3O_8 during heating experiments. Unit cells of U_3O_8 formed by heating samples low in U^6 are distinctly smaller than those formed from pitchblendes that are highly oxidized. These observations support view that composition of U_3O_8 structure is not constant; that U_3O_8 structure exists over solid solution range. Contrary to case of UO_2 structure, solution of oxygen in the U_3O_8 structure increases cell size, expansion being confined largely to "a" dimension. Confirmed by reduction of UO_3 to U_3O_8 in vacuum. An "X" phase was obtained which in many respects is similar to structures reported for U_2O_5 but which cannot be positively identified as such. Some considerable discussion of this phase is included. See also abst. No. 645.

469. PREPARATION OF REFRACTORIES FROM URANIUM DIOXIDE, R. E. Corwin and G. B. Eyerly. AECD-3349 (ANL-HDY-703), declassified Apr. 22, 1952.

Both pressing and slip casting used for forming UO_2 refractories. UO_2 should not be left in contact with dies or metal containers any longer than necessary, to avoid corrosion. After shapes have dried for several days at room temperature, they are fired in H_2 atmosphere in Mo-resistance furnace to a maximum temperature of 1750°C. Furnace must be cooled to 50°C before refractories are removed, to prevent oxidation. Variation in density of finished refractory with firing temperatures is shown graphically. Shrinkage averages about 14 to 15%. Precautions must be taken against getting UO_2 into body (physical cleaniness).

3.1 Additional references not abstracted

"Chemical and mineralogic studies on uranium," M. M. Klaproth. Mem. Akad. Wiss. Berlin 273 (1789).

"Beitrage zur Chemischen Kenntnis der Mineralkorper,"Anon, Berlin, 1797, Vol. 2.

"On the electrolytic conductivity of halogen compounds," W. Hampe. Chem. Ztg. **12**, 106 (1888).

"Preparation and specific gravity of crystallized uranium dioxide," W. F. Hillebrand. U. S. Geol. Survey Bull. No. 113, (1893). See also Z. anorg. Chem. **3**, 243 (1893).

"Uranous oxide," F. W. Oechsner de Coninck. Bull. classe sci. Acad. roy. Belg. 744 (1909).

"On several reactions of calcium oxalate," F. W. Oechsner de Coninck and A. Raynaud. Bull. soc. chim. France **9**, 301 (1911).

"New determination of the atomic weight of uranium," P. Lebeau. Compt. rend. **155**, 163 (1912).

"Revision of the atomic weight of uranium," O. Honigschmid. Compt. rend. **158**, 2004 (1914).

"Catalytic splitting of allyl alcohol; action of various oxides," P. Sabatier and B. Kubota. Compt. rend. **173**, 212 (1921).

"On the preparation of pure uranium," W. Jander. Z. anorg. allgem. Chem. **138**, 321 (1924).

"The equilibrium for the reduction of chromium sesquioxide and uranium dioxide with carbon, also the action of nitrogen on uranium carbide," O. Heusler. Z. anorg. allgem. Chem. **154**, 353 (1926).

"A critical study of the methods for the determination of uranium," R. Coomans. Ing. chim. **10**, 213 (1926).

"Process of producing uranium tetrabromide," J. M. Carter. U.S. Patent Number 2,469,916, May 10, 1949; assigned to U. S. AEC.

"Some wetting properties of metal powders," B. Kopelman and C.C. Gregg. Trans. Amer. Soc. Metals **41**, 293 (1949).

4. U_2O_5 (500-505)

500. ON THE CHEMICAL NATURE OF URANIUM AND SOME OF ITS NEW COMPOUNDS, B. Drenckmann. Z. ges. Naturw. **17**, 113 (1861).

$UO_3.2H_2O$ prepd. by heating finely powd. mixt. of U_3O_8 with excess $KClO_3$ in Pt crucible and repeatedly leaching melt with water. When $UO_3.2H_2O$ is heated for two or three hours in dry air at 80°C, it goes to monohydrate; however, reaction will not go in stagnant air under 160°C. Prepn. and properties of material which is U_2O_5 is discussed. Attempts to prep. UO_4 by strong oxidation of acid, neutral or alk. soln. of uranic acids, and uranates are reported, all attempts were unsuccessful.

501. RESEARCH ON THE SULFUR COMPOUNDS OF URANIUM, A. Remele. Ann. Physik Chem. (Pogg.) **124**, 114 (1865).

Question is raised concerning actual existence of compound reported as U_2O_5. Description is included of physical appearance of U_3O_8. Described as dark green to olive green or black. Color is influenced by decomposition and ignition temperatures.

502. ACTION OF NITRIC OXIDE ON METALS AND ON METALLIC OXIDES, P. Sabatier and J. B. Senderens. Compt. rend. **114**, 1429 (1892).

UO_2 was not noticeably affected by light. NO will react with brown UO_2 below red heat with evolution of light and formation of black U_2O_5.

503. RADIOACTIVITY OF URANIUM, C. Staehling. Compt. rend. **169**, 1036 (1919).

Experiments relating to radioactivity of "black" and "green" oxides of U. In addition to penetrating radiation, emit very soft radiation which forms basis of investigation. Demonstrated consistently, that even when black oxide U_2O_5 and green oxide U_3O_8 are prepd. from same sample of uranyl nitrate by direct method of calcination, soft radiation is always greater from black oxide than from green; penetrating radiation being same in both. If less active green oxide is reconverted into nitrate and subsequently converted into black oxide, it is always found to have increased in activity [as measured by soft (or total) radiation]. Other expts. of this nature are described, with substantially same result.

504. RADIOACTIVITY OF OXIDES OF URANIUM, C. Staehling. Compt. rend. **173**, 1468 (1921).

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Continuation of author's earlier experiments. Certain peculiarities in behavior of red and black oxides of U explained. Shown that red U oxide, even in state of great purity, "hydrates" slowly in air, without change in external appearance. Hydration only become appreciable after several mos. and may go on for several years. Phenomenon explains remarkable radioactive behavior previously observed, for by decreasing superficial density of U layer, it affects absorption of alpha rays. Black oxide is, however, not hygroscopic; this behavior explains why its apparent radioactivity does not diminish. Results thus obtained afford complete explanation of apparently anomalous behavior of red oxide.

505. THE CRYSTAL STRUCTURES OF SOME THORIUM AND URANIUM COMPOUNDS, N. C. Baenziger. AECD-3237, ISC-99, Oct. 15, 1948, declassified Sept. 11, 1951.

Complete structure determinations reported for U_2O_5, and U_3O_8. Structures of some compounds considered from viewpoint of theory of metals. New method of determing intensities of x-ray diffraction maxima from their photographic record developed which involves radioactive toning of film. Method appears to be almost as accurate as ionization-chamber method. Measurement of approximately 10 reflections can be determined per hour with an accuracy of better than 5%.

4.1 Additional references not abstracted

"Uranium oxides," F. W. Oechsner de Coninck and A. Raynaud. Bull. soc. chim. France **11**, 1037 (1912).

5. U_3O_8 (600-645)

600. RECHERCHES PHYSICO-CHIMIQUE, T. Guy-Lussac. Paris, 1811, Vol. I. pg. 262.

U_3O_8 can be reduced to UO_2 by K at about 150°C. Dull glow is produced during reductions.

601. RESEARCH ON URANIUM, E. Peligot. Ann. chim. phys., **12**, 549 (1844).

U_3O_8 can be prepd. from uranyl nitrate by carefully drying nitrate over an open flame and heating pulverized residue in oil bath to 250°C until acid vapors are no longer evolved.

602. ON THE APPLICATION OF AMMONIUM CHLORIDE IN ANALYTICAL CHEMISTRY, H. Rose. Ann. Physik Chem. (Pogg.) **74**, 562 (1848).

$UO_2(NO_3)_2.6H_2O$ can be converted to U_3O_8 by ignition with NH_4Cl.

603. ON THE ACTION OF WATER VAPOR ON METAL CHLORIDES AT HIGH TEMPERATURE. H. Kunheim. Dissertation, Univ. of Gottingen, 1861.

U_3O_8 obtained when UCl_4 is ignited in presence of water vapor.

604. THE SPECIFIC HEAT OF URANIUM OXIDE AND THE ATOMIC WEIGHT OF URANIUM, J. Donath. Ber. **12**, 742 (1879).

Pure uranyl acetate may be reduced to UO_2 in stream of H_2 and, when product is treated with HNO_3, can be ignited to U_3O_8. Mean specific heat of U_3O_8 between 0° and 100°C is 0.7979.

605. RESEARCH ON URANIUM. THIRD REPORT FROM HIS POSTHUMOUS WORK BY G. ALIBEGOFF AND G. KRAUSS. J. L. C. Zimmermann. Ann. **232**, 273 (1886).

Atomic weight of U is determined. Sodium uranyl acetate is prepd. by treating pure uranyl nitrate with Na_2CO_3 and excess boiling HOAc. Microcryst. product dried at 120° to 150°C. Discussion of conversion of U_3O_8 of ppt. obtained by treating U-contg. soln. with NH_3. If conversion is done in current of O_2, oxide does not have uniform composition; therefore, should first be reduced to UO_2 in current of H_2 and dtn. make on basis of that cpd. U_2O_5 reported by some investigators is mostly U_3O_8 with certain amount of UO_2. Pure U_3O_8 obtained by igniting purest possible uranyl salts to U_3O_8, reducing raw product with H_2 to UO_2, and reoxidizing with pure O_2 to U_3O_8. Product should cool in stream of O_2. Color of resulting material, which may be olive green to black, is influenced strongly by method of prepn. and heat of reduction. When

U_3O_8 is ignited and cooled quickly in air, will lose small quantities of O_2. Losses are greatly increased if cooling takes place in gas such as N_2 or CO_2 which are inert. When U_3O_8 is ignited in such atmospheres brown UO_2 is obtained. Green liquid is obtained with HCl when U_3O_8 is dissolved in closed system (temp. approx. 200°C). Completely converted to uranyl and U^4 sulfate when heated with concd. H_2SO_4 for a long time.

606. POTASSIUM CHLORATE, W. R. E. Hodgkinson and F. K. S. Lowndes. Chem. News 58, 309 (1888).

When U_3O_8 is heated with $KClO_3$ reaction involves loss of O_2 with evolution of a great deal of Cl_2 and formation of K_2UO_4. Reaction was found to begin at approximately 390°C.

607. THE DECOMPOSITION OF POTASSIUM CHLORATE IN CONTACT WITH METALLIC OXIDES, W. R. E. Hodgkinson and F. K. S. Lowndes. Chem. News 59, 63 (1889).

When U_3O_8 is heated with $KClO_3$ reaction involves loss of O_2 with evolution of a great deal of Cl_2 and formation of K_2UO_4. Reaction was found to begin at approximately 390°C.

608. THE INFLUENCE OF DIFFERENT OXIDES ON THE DECOMPOSITION OF POTASSIUM CHLORATE, G. J. Fowler and J. Grant. J. Chem. Soc., 57, 272 (1890).

When U_3O_8 is heated with $KClO_3$ reaction involves loss of O_2 with evolution of a great deal of Cl_2 and formation of K_2UO_4. Reaction was found to begin at approximately 390°C.

609. A FURTHER EXAMPLE OF ISOMORPHISM OF THORIA AND URANIUM DIOXIDE, W. F. Hillebrand. U. S. Geol. Survey Bull. No. 113, (1893).

Crystalline mixture of Th-U oxide can be prepared by mixing U_3O_8 and ThO_2 with borax glass in Pt crucible and fusing. When only U_3O_8 is fused oxyhedral crystals consisting of UO_2 accompanied by some UO_3 are obtained. UO_3 present will decrease as fusion continues. Crystals of UO_2 are found to be isomorphous with ThO_2 as determined by preparation of synthetic mixtures.

610. ON THE PREPARATION OF URANIUM AT HIGH TEMPERATURES, H. Moissan. Compt. rend. 116, 347 (1893).

Discussion on reduction of U_3O_8 to U metal using sugar-derived C. Impurities found were carbon (13.5 to 2.06 %) and N.

611. URANIUM OXYNITRIDE AND URANIUM DIOXIDE, E. F. Smith and J. M. Matthews. J. Am. Chem. Soc. 17, 686 (1895).

When U_3O_8 is mixed with large excess of NH_4Cl, placed in porcelain crucible, and heated with charcoal for 6 hrs. at white heat, reddish-brown product is obtained which contains neither N nor Cl.

612. PREPARATION AND PROPERTIES OF URANIUM, H. Moissan. Ann. chim. phys. 9, 264 (1896).

Uranium metal is more volatile than iron metal. Preparation of U_3O_8 by ignition of uranyl nitrate, which is easy to obtain pure, is discussed. Ignition is carried out in porcelain crucible.

613. NEW METHODS OF PREPARING SEVERAL OXIDES OF URANIUM, F. J. Aloy. Bull. soc. chim. France. 23, 368 (1900).

When UO_2 is exposed to air, slow oxidation takes place in which U_3O_8 is formed. Reduction, at 900° to 1200°C, of damp or dry UO_3 or U_3O_8 in a stream of H_2 will yield very pure UO_2. UO_2 can also be obtained by heating U_3O_8 in vacuum at 2000°C. Forms as rhombic platelets with flattened corners.

614. ON THE PREPARATION OF URANIUM, J. Aloy. Bull. soc. chim. France 25, 344 (1901).

Attempts to reduce U_3O_8 with C at current density of 25 amps. did not give complete reduction; 100 amps. at 50 to 60 v. were required.

615. THE COLORING POWER OF URANIUM OXIDE IN GLAZES OF VARIOUS COMPOSITION, F. H. Riddle. Trans. Am. Ceram. Soc. 8, 210 (1906).

Coloring power of U oxide in six typical glaze compositions is investigated. Content of coloring oxide was varied from 0.003 to 0.005 equivalents, added to formula weight of glaze, corresponding to average range of from 0.78 to 12.9% of U_3O_8, in terms of dry glaze. U oxide produces rich orange shades in all glazes high in PbO while in such glazes low in or free from Pb, characteristic lemon-yellow tints are obtained. Presence of H_3BO_4 intensifies lemon color. Fritted glazes take up more U oxide in soln. than raw glazes. Content of 0.05 equivalent of U oxide is entirely too great and 0.02 equivalent seems to be limit corresponding to an average content of 5.17% of U_3O_8.

616. UEBER DIE REDUKTION DER METALLOXYDE DER CHROMGRUPPE MITTELST WASSERSTOFFS IN DER HOCHSPANNUNGSFLAMME, E. Faehr. Dissertation, Univ. of Munich, 1908.

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UO_2 may be obtained as the end-product when U_3O_8 is reduced with H_2 in the high-voltage flame. U oxides with ratio of more than 2.61 atoms of O per U cannot be volatilized because of high-vapor pressure of O in compound.

617. THE PREPARATION OF URANIUM, F. Giolitti and G. Tavanti. Gazz. chim. ital. **38**, II, 239 (1908).

Prepn. of U, reduction of its oxides with Al is considered. "pure" uranyl salts available in commerce for prepn. of U_3O_8 always contain alk. in form of double salts. Thus, pure uranyl acetate of Merck and Kahlbaum corresponds to $UO_2(C_2H_3O_2)_2.Na(C_2H_3O_2).2H_2O$ and give Na pyrouranate, $Na_2U_2O_7$ on ignition. To remove alk. proceed: (1) ignite mass containing alk. pryouranate in stream of H_2, extract reduction product with H_2O; or (2) dissolve ignition product containing pyrouranate in acid (HNO_3) and transform into pure NH_4-uranate by repeated pptns. with NH_3. Latter, on ignition, gives pure U_3O_8 which cannot be obtained by method (1). Importance of observations in analytical determinations is pointed out. Method of Moissan [Compt. rend. **122**, 1302 (1896)] in which Al is used is not suitable for prepn. of metallurgical U nor its alloys. Goldschmidt method, modified by Stavenhagen [Ber. **32**, 3065 (1899), and Ber. **35**, 909 (1902)] was fairly successful.

618. THE PREPARATION OF URANO-URANIC OXIDE, U_3O_8, AND A STANDARD OF RADIO-ACTIVITY, H. N. McCoy and G. C. Ashman. Am. J. Sci. **26**, 521 (1908).

Radioactive substances accompanying U in minerals are almost completely removed by ordinary process of prepn. of so-called chemically pure $UO_2(NO_3)_2$. Minute traces of Ra may be removed by means of $BaSO_4$. Pure U_3O_8, of perfectly definite composition, is readily obtained by heating nitrate or any lower or higher oxide of U in air at 700°C.

619. HEAT OF FORMATION OF THE OXIDES OF VANADIUM AND URANIUM, AND EIGHTH PAPER ON HEAT OF COMBINATION OF ACIDIC OXIDES WITH SODIUM OXIDE, W. G. Mixter. Am. J. Sci. **34**, 141 (1912).

Continuation of work, making use mainly of Na_2O_2 to carry out reactions. Inability to prepare pure V left results subject to some uncertainty. Among results are $3U + 4O_2 \rightarrow U_3O_8 + 845{,}200$ cal.; $U + 3O \rightarrow UO_3 + 303{,}900$ cal.; $UO_3 + Na_2O \rightarrow Na_2UO_4 + 96{,}000$ cal.; and $U_3O_8 + \frac{1}{2}O_2 \rightarrow 3UO_3 + 16{,}200$ cal.

620. MEASUREMENT OF SPECIFIC HEAT AT LOW TEMPERATURES, A. S. Russell. Physik. Z. **13**, 59 (1912).

By means of Nernst-Koref—Lindemann Cu calorimeter mean sp. heats were detd. over approx. ranges 45° to 0°, 0° to -78°, and -78° to -190°C for U_3O_8 and other salts. From data conclusion is drawn that Kopp's law does not hold at low temp., where Dulong and Petite rule is invalid. Expressed in terms of new theories of specific heat, frequency of vibration of atom in compound is not same as in free state. Most striking illustration of this failure of Kopp's law is fact that molal heat capacity of SiC at 138° Absolute is less than the atomic heat of Si.

621. DAS ELEKTROCHEMISCHE VERHALTEN DES URANS UND EINIGER URANVERBINDUNGEN, E. Rideal. Dissertation, Univ. of Bonn, 1913.

Description of reduction of U_3O_8 by Na and Mg in presence of $CaCl_2$ is given. Metal of 99.4 to 99.6% U was obtained.

622. THE REDUCTION OF URANIUM OXIDE, E. K. Rideal. J. Soc. Chem. Ind. (London) **33**, 673 (1914).

Several methods for reduction of U_3O_8 were tried. Best results were obtained by electrothermal-thermite process. Granular resistor used to heat tube of pure MgO which contd. mixt. of 80% U_3O_8 and 20% Mg powder pressed into form of rods. Ends of rods were placed in contact with C electrodes and current of H_2 passed through apparatus. When rods were hot enough to become conducting, main electrodes were connected to 110-volt circuit, causing an arc of Mg vapor which reduced oxide to metal. H_2 was displaced by CO_2 and MgO removed from product by washing with dil. acetic acid. Yield of 98-99% metal was obtained. Good reduction was also obtained by heating mixt. of 50% U_3O_8, 15% $CaCl_2$, 15% Mg, and 20% Na in steel cylinder to bright-red heat.

623. THE REDUCTION OF METALLIC OXIDES WITH HYDROGEN AT HIGH PRESSURES, E. Newbery and J. N. Prign. Proc. Roy. Soc. (London) **A92**, 276 (1916).

U_3O_8 will not be reduced by H_2 any further than UO_2 when heated as high as 2500°C at pressures up to 150 atmospheres.

624. PURIFICATION OF URANIUM COMPOUNDS, E. Wilke-Dorfurt. Wiss. Veroffentl. Siemens-Konzern **1**, 143 (1920).

Discusses prepn. of U_3O_8 and mentions that classical method which used uranyl nitrate extraction with Et_2O contains disadvantage of danger of explosion during purification process. Proposes

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that alk.-free U_3O_8 cannot be obtained by this method. Alk.-free products obtained by recrystg. nitrate several times in H_2O as follows: slight excess of carbonate-free NH_3 is added and soln. is satd. with H_2S. Then, heated to boiling without interruption of H_2S and ppt. is washed well with water contg. $(NH_4)_2S$, sucked dry in filter and dissolved in small quantity of concd. HCl. Dark-green UCl_4 is formed. H_2S is driven off by boiling the soln., and further treatment with NH_3 and H_2S is made. UCl_4 soln. is again pptd. with NH_3 and ppt. again dissolved in strong HNO_3. Uranyl nitrate formed is recrystd. from pure H_2O until no free acid remains, and then ignited in normal manner to U_3O_8.

625. THE RELATIVE ACTIVITIES OF RADIOACTIVE SUBSTANCES IN AN UNCHANGED PRIMARY URANIUM MINERAL, W. P. Widdowson and A. S. Russell. Phil. Mag. **46**, 915 (1923).

Pitchblende was mineral used in investigation. Method of prepn. pure U_3O_8 for comparison was given.

626. THE ROLE OF WATER IN THE REACTIONS OF SOLID SUBSTANCES, D. Balarev. Z. anorg. allgem. Chem. **136**, 216 (1924).

U_3O_8 and BaO were found to react quite violently when heated to 328°C. Temp. at which reaction begins apparently depends upon how tightly mixture is compacted, but cannot begin any higher than 360°C.

627. SYSTEMATIC AFFINITY PRINCIPLES. XLI. ON URANIUM OXIDE, W. Biltz and H. Muller. Z. anorg. allgem. Chem. **163**, 257 (1927).

UO_3 was prepd. from $UO_4.xH_2O$ as orange amorph. material. U_3O_8 prepd. below 800°C is moss-green; above that temp. is black. UO_2 is brown or dark brown-violet. System UO_3-U_3O_8 is fully discussed. Direct inversion of U_3O_8 into UO_3 is probable in minerals, it is proved for prepns. Observed pressures are not equil. pressures, but are near to them. System UO_3-U_3O_8 is reversible. Discussion of mol. vol. and relations between color and cryst. form is included.

628. URANIUM OXIDE COLORS AND CRYSTALS IN LOW TEMPERATURE GLAZE COMBINATIONS, J. R. Lorah. J. Am. Ceram. Soc. **10**, 813 (1927).

General color effect produced by uranium with the following compounds: CeO_2—dirty green colors, fusion usually incomplete;

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CoO—greens and blue greens; CuO—dark green; Fe_2O_3—reddish brown to very dark brown; $Mn(OH)_2$—dark brown to almost black; TiO_2—brown, fusion usually incomplete; $NiCO_3$—green spots, does not seem to disperse with main portion of glaze; SnO_2—infusible in these mixtures; ZnO—small amount acts as flux and lightens color; CaF_2—does not affect color, large amounts act as refractory; $CaCO_3$, $BaCO_3$, $MgCO_3$—do not affect color, large amounts act as refractory; Na_2CO_3, K_2CO_3, Li_2CO_3—act as fluxes and lighten colors in lead glazes. When silica, but no lead, is present they produce only yellow colors. Tend to produce glassy structure and bad crazing; $Bi(OH)_2$ and $CdCO_3$—intensify or may even darken orange color; and MoO_3 and K_3VO_4—produce pink and yellow shades. Glazes containing either borax or boric acid with silica give yellow glazes with greenish tinge and show no tendency toward formation of any orange color. Using only uranium oxide in lead glaze, shade from light yellow to deep orange or almost a red may be obtained by simply varying quantity; 5% will produce bright orange and 10% dark orange, higher percentage seeming to darken color very little. If percentage is sufficiently increased it also acts as refractory. Black spots are undoubtedly due to reduction of large masses of yellow uranium oxide to black oxide (UO_2) by some gases produced from combustion of oil used to fire furnace. It can not be due to high temperatures alone, since all oxides of uranium are changed to yellow form (U_3O_8) upon being heated to high temperatures in presence of air. Found considerable evidence of crystalline glazes and some discussion of habit and form of crystals but no attempt made to identify various crystalline forms according to composition, etc.

629. A short discussion with fourteen early references on colors produced by uranium oxides in ceramic glazes. In collected writings of Seger uranium oxide is mentioned as producing yellow colors. Riddle studied coloring power of uranium oxide in glazes of various compositions. Koerner first noticed tendency of lead-uranium and bismuth-uranium mixtures to form crystals. Akatsuka also obtained crystalline glazes. Wilson produced good high-temperature greens from certain uranium-cobalt combinations. Montgomery and Krusen produced brilliant jet blacks under reducing conditions. Howe produced yellow underglaze colors by use of soluble salts of uranium. Minton, Radcliffe, Larkin, Binns and Lyttle, Akatsuka, Wolfram and Harrison, and Mathiasen have produced yellow, orange,

brown, and red colors. An anonymous article gives a very good summary of knowledge concerning uranium glazes up to time of publication.

Hermann A. Seger, Collected Writings.

F. H. Riddle, Trans. Am. Ceram. Soc. **8**, 210 (1906).

J. Koerner, Trans. Am. Ceram. Soc. **10**, 61 (1908).

Mikiya Akatuska, Ceram. Abs. **2**, 142 (1923); Report of the Pottery Laboratory (Kioto) **1**, 57 (1922).

H. Wilson, J. Am. Ceram. Soc. **1**, 238 (1918).

E. T. Montgomery and I. A. Krusen, Trans. Am. Ceram. Soc. **16**, 335 (1914).

R. M. Howe, Trans. Am. Ceram. Soc. **16**, 487 (1914).

L. H. Minton, Trans. Am. Ceram. Soc. **9**, 777 (1907).

B. S. Radcliffe, Trans. Am. Ceram. Soc. **16**, 209 (1914).

P. G. Larkin, J. Am. Ceram. Soc. **1**, 429 (1918).

C. F. Binns and F. Lyttle, J. Am. Ceram. Soc. **3**, 913 (1920).

H. G. Wolfram and W. N. Harrison, J. Am. Ceram. Soc. **7**, 857 (1924).

O. E. Mathiasen, J. Am. Ceram. Soc. **7**, 499 (1924).

Anon., Ceram. Abs. **2**, 172 (1923); Chem. Trades J. and Chem. Eng. **72**, 570 (1923).

630. THEORY OF ORDERED MIXED PHASES, C. Wagner and W. Schottky. Z. physik. Chem., B, **11**, 163 (1931).

Discusses theory of ordered mixed phases in oxides as exemplified by U_3O_8.

631. CONTRIBUTIONS TO THE DATA ON THEORETICAL METALLURGY. I—THE ENTROPIES OF INORGANIC SUBSTANCES, K. K. Kelley. Washington, U. S. Bur. Mines, Bull. 350, (1932).

Values for entropy at 298.1°K are given for U and U_3O_8 and as many other materials as necessary data was found. Methods of calcn. are discussed and a bibliography of 400 references is included.

632. STUDIES OF THE PROMOTING ACTION OF A CATALYST PROMOTER AND CARRIER, II, S. Tsutsumi. J. Chem. Soc. Japan **58**, 63 (1937).

Effect of calcining temperature upon gas-absorbing power of mixtures Co + Cu + U_3O_8 in range 200° to 300°C, and Co + U_3O_8 and Co + ThO_2 in the range 250° to 450°C contg. various amounts of diatomaceous earth was studied. Gas used was mixture CO + H_2 in ratio 1:2. Proper temp. of max. absorbing power does not change much with amount of diatomaceous earth.

633. X-RAY POWDER PATTERNS OF SOME U METAL COMPOUNDS, H. S. Peiser and T. C. Alcock. BR-589, Mar. 19, 1945, declassified Oct. 2, 1946.

X-ray patterns are given in tabular form for UO_3, U_3O_8. Discussion of structure of UC and proposed new value of the metallic radius of U atom is included.

634. SOME STUDIES OF THE REACTIONS OF URANIUM OXIDES WITH HYDROGEN, OXYGEN, AND WATER, D. M. Gillies. MDDC-647, June 1946, declassified Feb. 7, 1947.

To obtain data that would be useful in predicting changes that might be expected to occur in oxidation state and degree of hydration of powdered U oxides maintained for long periods of time at temperatures between 30° and 300°C in presence of excess water, hydrogen, oxygen, and possibly H_2O_2. Reaction of hydrogen and oxygen with water slurries of U_3O_8 were studied at 100° to 300°C. Rates of reactions appear to fit an equation of form $-d(1 - x)/dt = kp^n (1 - x)^\theta$, where x is fraction of U^{+6} or U^{+4} which has been reduced or oxidized, resp., at time t, n is order of reaction with respect to pressure, p, of reacting gas. Exponent theta, "order" of reaction with respect to solid oxide, is thought of as measure of decrease of solid surface with time, difficulty encountered by gas molecules in penetrating solid particles, or some equivalent phenomenon. Oxidation reaction appears to be first order with respect to O_2 (experimentally n equals 1.14), and value of theta for particular oxide preparation used, was 3.7. Activation energy was computed to be 13,000 cal (10%). Value of theta for reduction reaction, using same oxide, was 15.0. Assuming reaction to be first order with respect to hydrogen, activation energy is 10,000 cal (15%). U_3O_8 suspended in water is oxidized much more rapidly that it is reduced. Under 14 atms. of oxygen oxidation reaction is 76% complete in 2 hours at 250°C, under 16.4 atms. of hydrogen reduction reaction is only 5 to 6% complete in 2 hours at 250°C. Difference in rate is due largely to difference in theta for two reactions; that is, rate of reduction reaction decreases more rapidly with decrease in "available oxide surface" than does rate of oxidation reaction. $UO_3.H_2O$ was

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reduced even more slowly than U_3O_8, possibly because crystal size was much greater. Results indicate that U oxide—water mixture exposed to hydrogen and oxygen at pressures of similar magnitude, U would drift toward U^{+6}. Thermal decomposition of $UO_4.2H_2O$ in presence of water, giving hydrated UO_3 and O_2, was studied as function of temp. At 61°C, reaction is detectable but very slow; at 100°C, half-life is about 400 hours; at 185°C, reaction is essentially complete in 1 hr. Assuming either first- or second-order process, activation energy is 30,000 cal (10%). Thermal stability of hydrates of UO_3 in presence of water was investigated. Highest hydrate, $UO_3.2H_2O$, is stable up to at least 61°C. Transition to $UO_3.H_2O$ occurs between 61° and 77°C. At 265°C, monohydrate seems to be stable, but at 300°C it slowly loses water. At 350°C crystalline hemihydrate, UO_3,H_2O, is formed. Previously unreported polymorphic forms of hydrates exist. Different forms were obtained by reaction of two different forms of anhydrous oxide with H_2O. Two forms of dihydrate were found; both were microcrystalline, but x-ray patterns of two were distinct. At least two forms of monohydrate exist, rhombic form and triclinic form. Hemihydrate is definite crystalline compound, probably monoclinic. Crystalline monohydrate reacts with water extremely slowly and can exist in liquid water for long periods at temperatures where dihydrate is thought to be stable. Evidence is presented to support conclusion that in dihydrate one mole of water is present as zeolitic water. Anhydrous UO_2 and U_3O_8 were not found to react with water.

635. THE CONVERSION OF UF_4 TO U_3O_8, A. D. Tevebaugh, R. D. Tevebaugh, W. E. Cline, and J. C. Warf. MDDC-1526, declassified Dec. 23, 1947.

Methods of conversion of UF_4 to U_3O_8 by fusion with $(NH_4)_2C_2O_4.2H_2O$ and other salts are described. Pyrohydrolytic method is described whereby mixture of steam and air at 800°C is used to convert UF_4 to U_3O_8.

636. THE IGNITION OF U_3O_8 IN OXYGEN AT HIGH PRESSURES AND THE CRYSTALLIZATION OF UO_3, S. Fried and N. R. Davidson. MDDC-1659, June 25, 1945, declassified Jan. 29, 1948.

U_3O_8 or amorphous UO_3 heated in oxygen under pressure of 30 to 150 atms. at temp. of 500° to 750°C are converted to crystalline UO_3, three varieties are formed. Least stable is hexagonal UO_3,

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crystal structure very closely related to U_3O_8. Most stable phase is isomorphous with UO_3 prepared by Mallinckrodt Chemical Co. by calcining $UO_2(NO_3)_2$. Different varieties of UO_3 show markedly different stabilities with regard to decomposition into lower oxides in presence of oxygen under 1 atmosphere pressure at 600° to 800°C. Most stable UO_3 phase remains unchanged at 700°C but decomposes to U_3O_8 at 800°C. Less stable, amorphous UO_3 decomposes at 620°C to $UO_{2.959}$, tan color; at 625° to 630°C, is reduced to $UO_{2.82}$; and at 650°C decomposition is essentially complete to U_3O_8. Observations appear to explain vastly discrepant reports in literature as to temperature at which UO_3 decomposes to U_3O_8. Samples of UO_3 prepared elsewhere by vapor phase oxidation of U_3O_8 with HNO_3 gave x-ray patterns different from those of any of 3 phases prepared by ignition of U_3O_8 in O_2 under high pressure. One sample when treated at 600°C with O_2 at atmospheric pressure "disproportionated" into mixture of U_3O_8 and "Mallinckrodt" UO_3.

637. CRYSTAL STRUCTURE OF URANIUM OXIDE (U_3O_8), F. Gronvold. Nature 162, 70 (1948).

Single U_3O_8 crystals could not be prepared; however, one preparation gave X-ray photographs in which reflections with indicies (001) only were sharp and well defined. From this a hypothetical crystal structure was formulated. Cell is orthorhombic with dimensions a= 6.703 kX; b= 3.969 kX; c = 4.136 kX. Density of U_3O_8 is 8.34 g/cc. Elementary cell contains 2 U atoms. U_3O_8 structure is probably related to ReO_3 structure, but with deformed $(UO_6)^{-4}$ octahedrons with anion vacancies.

638. PURIFICATION OF URANIUM OXIDE, J. I. Hoffman. J. Wash. Acad. Sci. 38, 233 (1948).

U_3O_8 is obtained by heating purified uranyl nitrate at 1000°C. Uranyl nitrate is obtained by evaporating HNO_3 soln. of about 50 g. of impure oxide to dryness on steam bath, extracting residue with 100 ml of Et_2O containing 5 ml water, and removing uranyl nitrate from Et_2O phase by successive treatments with 20-ml portions of water. Method is applied to mixtures containing U_3O_8 and compounds of other elements especially those of rare-earth group, to pitchblende, and to carnotite. Spectrochemical tests of purified U_3O_8 for 64 elements showed only traces of Ag, Al, Ca, Cu, Fe, Mg, Mo, Na, and Si.

639. THERMOGRAVIMETRIC ANALYSIS OF PRECIPITATES. XXIV—DETERMINATION OF URANIUM, C. Duval. Anal. Chim. Acta., 3, 335 (1949).

Study of gravimetric methods for determination of U^{+4} and U^{+6}; two new forms of weighing are suggested, as oxalate and anhydrous oxinate. Table summarizes temperature limits, determined by means of Chevenard thermobalance, for various precipitates:

Pptg. reagent	Form weighed	Temp. limits, °C
Ammonium hydroxide................	UO_3	480 to 610
Ammonium hydroxide................	U_3O_8	745 to 946
Ammonia (gas).....................	U_3O_8	675 to 946
Pyridine..........................	U_3O_8	745 to 946
Ammonium benzoate.................	U_3O_8	691 to 946
Hexamethylenetetramine............	U_3O_8	745 to 946
Tannin............................	U_3O_8	570 to 878
Hydrogen peroxide.................	U_3O_8	811 to 946
Hydrofluoric acid.................	U_3O_8	811 to 946
Ammonium sulfate..................	U_3O_8	850 to 946
Disodium phosphate................	$U_2P_2O_{11}$	673 to 946
Oxalic acid.......................	$U(C_2O_4)_2$	100 to 180
Oxalic acid.......................	U_3O_8	700 to 946
Cupferron.........................	U_3O_8	800 to 946
Beta-isatoxine....................	U_3O_8	408 to 946
8-hydroxyquinoline................	$HUO_2(C_9H_6ON)_3$	< 157
8-hydroxyquinoline................	$UO_2(C_9H_6ON)_3$	252 to 346
Quinaldinic acid..................	U_3O_8	610 to 946

640. ON THE REVERSIBILITY OF THE REACTION $3UO_3 \leftrightharpoons U_3O_8 + O$, A. Boulle and M. Domine-Berges. Compt. rend. 228, 72 (1949).

Authors previous work [Compt. rend. 227, 1365 (1948)] formation of solid solution $UO_{2.90}$, stable at 520° to 610°C, was recognized as intermediate stage in decomposition of UO_3. Present paper conditions of reverse reaction are described, viz., of reoxidation of U_3O_8 and of solid solution. X-ray spectra of U_3O_8 revealed existance of two crystalline states, I and II; state I being obtained from state II by heating at approximately 575°C. Whereas a total reoxidation of II can be made through heating in air or in oxygen at 300° to 500°, state I does not reoxidize. Reoxidation of solid solution $UO_{2.90}$ could not be observed in experimental conditions used for other oxides.

641. ON THE ELECTROLYTIC PREPARATION AND PROPERTIES OF URANIUM BORIDES, J. L. Andrieux and P. Blum. Compt. rend. **229**, 210 (1949).

Earlier experiment by one author had shown that uranium boride, UB_4, could be formed by electrolysis of bath of molten borate and alkaline earth fluorides in soln. with quantity of U_3O_8 [Andrieux, Ann. chim. **10**, 423 (1929)]. Attempt was made to prepare new borides of U by varying concentrations of borate and U_3O_8 in bath and by substituting $MgFe_2$ for alkaline earth fluorides. In first attempts concentration of U_3O_8 was too great in respect to borate, and only UB_4 was formed. When concentration of U_3O_8 was reduced to as much as 1/40 to 2 moles of borate, there resulted a mixture of UB_4 with a new boride UB_{12}. Borides can be separated by use of concentrated HCl or H_2SO_4, since UB_4 is easily attacked by these while UB_{12} is very resistant to acids.

642. FINAL TECHNICAL REPORT, L. G. Bassett, S. E. Wiberley, and J. U. Shepardson. NYOO-98, Dec. 12, 1949.

Chemical analyses of standard sample of high-grade U ore; deviations were obtained by 4 different laboratories: National Bureau of Standards; Lucius Pitkin, Inc.; Ledous and Co.; and Mallinckrodt Chemical Works. Results are presented for comparison of established analytical methods for U_3O_8 used by these laboratories. Gravimetric procedure involving an extraction method for U was also used on same ore sample. Preliminary investigation of new rapid titrimetric procedure involving Hg cathode electrolysis as a means of eliminating interfering elements is reported.

643. THE DILATATION OF METALLIC OXIDES USED IN CERAMICS, M. J. Day. Bull. soc. sci. Bretagne **24**, 13 (1949), published Sept. 10, 1950.

Coefficients of expansion at low temperatures of alumina, zirconia, beryllia, rutile, quartz, magnesia, and uranium oxide determined by dilatometric methods over the range -130° to 50°C. Uranium oxide samples consisted of mixtures of U_3O_8 and UO_2 resulting from fritting at various temperatures of calcined $UO_2(NO_3)_2$. Coefficients for these samples were determined at 375°C. Transformations indicated by changes in coefficients of expansion were observed and discussed.

644. EXTRACTION OF URANIUM FROM ORE CONCENTRATE, H. Chr. Neeb and K. Stokland. Forsvarets Forskningsinstitutt Arbok, III, (1950-51).

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Uranium for Kjeller pile was obtained from uraniferous pegmatite deposit at Einerkilen in Evje in Setesdal, Norway. Process used to obtain pure U_3O_8 from ore concentrate is discussed. Ore was treated with warm dilute HNO_3, Ra was pptd. with Na_2SO_4 after addition of $Ba(NO_3)_2$, and U was pptd. as ammonium uranate, which was transformed to U_3O_8 at over 1000°C. Engineering problems involved in acid treatment of concentrate, slurry filtration, Ra removal, filtration of uranate, and ignition to oxide are discussed.

645. STUDIES OF RADIOACTIVE COMPOUNDS: III-URANO-URANIC OXIDE (U_3O_8), I. H. Milne. Am. Mineral. 36, 415 (1951).

Weissenberg films of U_3O_8 crystals prove existence of two hexagonal cells whose axis of reference coincide in direction; dimensions, a= 3.93, c= 4.14 kX (cell contents 1/3 U_3O_8) and a= 3.86, c= 4.14 kX. Powder photographs indicate large cell is always present. Suggested that "two cell" phenomenon is due to introduction of oxygen into portion of structure. Oxygen may be either in state of solid solution or in chemical combination necessiating change of some U^{+4} to U^{+6}. Space group assigned C6mmm. Hexagonal cell contains 1/3(U_3O_8). Suggested that true hexagonal "c" dimension is actually 3 x 4.14 A, measured value being a strong pseudoperiod resulting from arrangement of uranium atoms in structure. Two suggestions offered to account for two-cell structure of U_3O_8; both depend upon introduction of oxygen into structure: may enlarge "a" dimension of cell, with higher oxide confined to outer boundaries of grains and crystals where solution of oxygen is most likely, or introduction of oxygen with its consequent change of U^4 ions to smaller U^6 ions, may result in a shrinkage of cell as it does in case of UO_2 structure. Suggestions called for two similar oxide structures with greater and less oxygen than resultant U_3O_8. See also abst. No. 468.

5.1 Additional references not abstracted

"Some observations on the preparation of urano-uranic oxide," K. von Hauer. Jahrb. geol. Reich. 4, 557 (1853).

"On the fluorine compounds of uranium," H. C. Bolton. Dissertation, Univ. of Gottingen, 1866.

"On some fluorine compounds of uranium," A. Smithells. J. Chem. Soc. 43, 125 (1883).

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"On the occurance of nitrogen and helium in uranium minerals," V. Kohlschutter. Ann. 317, 158 (1901).

"New investigation on the atomic weight of uranium," T. W. Richards and B. S. Merigold. Z. anorg. Chem. 31, 235 (1902).

"On several reactions of calcium oxalate," F. W. Oechsner de Coninck and A. Raynaud. Bull. soc. chim. France 9, 301 (1911).

"The preparation of pure uranium," E. Botolfsen. Bull. soc. chim. France. 45, 626 (1929).

"Method for the preparation of the standard uranium oxide and the determination of its saturation current," A. N. Puilkov. Zhur. Obschei Khim. 1, 133 (1931).

"Theory of ordered mixed phases," C. Wagner and W. Schottky. Z. physik. Chem. B11, 163 (1931).

"Deformable rare metals, vanadium, thorium, and uranium," W. Kroll. Z. Metallkunde 28, 30 (1936).

"The determination of U_3O_8 in Canadian ores by means of the 'Ten Per Cent' reductor," R. J. Heaney and C. J. Rodden. MDDC-901, May 26, 1946, declassified Apr. 29, 1947.

"The determination of small amounts of nitrate in U_3O_8 and other uranium oxides," E. Staple and others. MDDC-1564, July 23, 1946, declassified Dec. 9, 1947.

"The preparation of standard samples for field analyses," F. E. Senftle and C. R. Boyce. AEC NP-1602, Radiation laboratory topical report No. 25. Ottawa, Dept. Mines and Resources, June 7, 1949.

6. UO_3 (700-732)

700. ON THE COMPOUNDS OF PHOSPHORIC ACID AND ARSENIC ACID WITH URANIUM OXIDE. INVESTIGATON OF CHALCOLITH AND URANITE. PROPOSAL OF A NEW DETERMINATION METHOD FOR ARSENIC ACID, G. Werther. J. prakt. Chem. **43**, 321 (1848).

Prepn. of crystals of compound $UO_2H_4(PO_4)_2 \cdot 3H_2O$ is reported. Obtained by heating small amounts of H_3PO_4 with UO_3 to boiling and allowing to stand over H_2SO_4. Part of water in material is lost upon heating, and lusterless light-yellow powder is obtained. At red heat crystals puff up and lose remaining water but do not melt or give off H_3PO_4. Alk. soln. does not affect material but alk. fusion will decomp. it. Reduced to UO_2 when fused with carbonized potassium sodium tartrate.

701. ON THE SUBLIMATION OF SOME COMPOUNDS AT WHITE HEAT, L. Elsner. J. prakt. Chem. **99**, 257 (1866).

Yellow U oxide (UO_3) is volatile at approximately 2500° to 3000° C. Probably refers to decomp. product of UO_3 rather than to UO_3 itself.

702. ON THE SPECIFIC VOLUMES OF OXIDES, B. Brauner and J. I. Watts. Phil. Mag. **11**, 60 (1881).

Specific gravity (5.14) and specific volume (56.03) are reported for UO_3.

703. INVESTIGATIONS OF URANIUM, J. L. C. Zimmermann. Ann. **213**, 285 (1882).

If Zn is used to reduce soln. of $(UO_2)^{2+}$, reduction is carried to U^{3+} stage rather than stopping at U^{4+}. Red HCl soln. characteristic of trivalent state can be prepd. by reducing UO_2Cl_2 with Zn and HCl. Discussion of absorption spectra of U^{3+}, U^{4+}, and $(UO_2)^{2+}$ in aq. soln. Titration of U soln. after reduction to U^{3+} state with Zn-amalgam using $K_2Cr_2O_7$ and diphenylamine as an indicator is discussed. Method for prepg. pure UO_3 from commercial uranyl hydroxide using warm HCl soln. std. with H_2S to ppt. As_2S_3 and small amts. of other sulfides present is given. Filtrate is treated with NH_3 and excess $(NH_4)_2CO_3$ after warming with $(NH_4)_2S$. Ppt. formed is filtered off and soln. is acidified with HCl. Dissolved CO_2 is eliminated by boiling and U pptd. as chocolate-brown UO_2S by adding NH_3 and $(NH_4)S$. Ppt. is converted to oxide and raw U_3O_8 is dissolved in HNO_3, filtered, evapd. and crystd., and uranyl nitrate dissolved in Et_2O. Filtrate is then evapd. to dryness and residue ignited strongly. UO_3 will combine with bases forming uranates. UO_3 is slightly acid material in contrast to UO_2 which is strongly basic. Prepn., properties, and crystal characteristics of Li, K, and Na uranates and diuranates are discussed.

704. ON SILICON TETRACHLORIDE, G. Rauter. Ann. 270, 235 (1892).

When UO_3 is heated for about 8 hours in closed tube at 370° to 380°C. with $SiCl_4$, Cl_2 and a residue containing unchanged UO_3, UCl_4, UO_2Cl, and SiO_2 are obtained.

705. ACTION OF NITRIC OXIDE ON METALS AND METALLIC OXIDES, P. Sabatier and J. B. Senderens. Bull. soc. chim. France 7, 502 (1892).

Action of NO on UO_3 is compared with action of air (heat to 500°C). First yields black U_2O_5; second, yellow-brown U_3O_8.

706. ON OZONE FORMATION, O. Brunck. Z. anorg. Chem. 10, 222 (1895).

UO_3 prepd. by decomposition of nitrate at 300°C may be freed of N_2 by conversion to ammonium uranyl carbonate and then heating for approximately 24 hours in stream of air at 350°C. until litmus paper no longer shows any trace of base. UO_3 still will contain small traces of NH_3. Prolonged heating of UO_3 and CO_2 is reported to give a pure, mossy-green U_3O_8. Prolonged heating of UO_3 in O_2 will produce detectable amounts of O_3. When UO_3 is heated with $KClO_3$, K_2UO_4 and free Cl_2 are formed. When $UO_4.2H_2O$ is heated slowly in stream of CO_2 as high as 150°C, it will not lose H_2O and undergoes no visible change. Above 150°, however, will lose H_2O and O_2 and go to orange-yellow UO_3 without forming any ozone.

707. REDUKTION DURCH CALCIUM, A. Burger. Dissertation, Univ. of Basel. 1907.

UO_3 can be reduced smoothly in vacuum with Ca to a product (powder) 98.7 to 99.4% U.

708. TRIBO LUMINESCENCE OF URANIUM. A. C. G. Egerton. Nature 85, 308 (1911).

Crystals of $UO_2(NO_3)_2.6H_2O$ show a light-greenish-yellow tribo luminescence. Author disagrees with earlier writers which report tribo luminescence for crystals of uranyl acetate. Tribo luminescence reported for UO_3 by Rudge is said to be characterized

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as an oxidation phenomenon. Discussion included on oxidation of uranium powder and on burning U powder in flames.

709. URANIC ANHYDRIDE AND ITS HYDRATES, P. Lebeau. Compt. rend. **154**, 1808 (1912).

UO_3, prepd. in usual way, contains H_2O and N_2; to obtain pure compound it is necessary to heat for some time at 500°C. in current of O_2. In contact with H_2O vapor, UO_3 is rapidly transformed into $UO_2(OH)_2$.

710. THE HYDRATES OF URANIC ANHYDRIDE AND THE HEAT OF FORMATION OF URANYL NITRATE, M. de Forcrand. Compt. rend. **156**, 1954 (1913).

Monohydrate is quite stable and may be formed by allowing anhydride to remain in moist atm. for short time. Dihydrate is formed by allowing UO_3 to remain in moist atm. for several days, it loses 1 mole of water in H_2SO_4 desiccator. Heats of simple dehydration and of dehydration accompanied by decomposition are almost same, so that dehydration cannot be accomplished without decomposition. Heats of combustion of U and UO_2 are discussed.

711. STUDY OF SOME RAPID LOW-TEMPERATURE OXIDE REACTIONS BY MEANS OF HEATING CURVES, J. A. Hedvall and N. vonZweigbergk. Z. anorg. allgem. Chem. **108**, 119 (1919).

Formation of a compound of BaO with UO_3 was indicated. Lists host of other oxides reacted with BaO.

712. SYSTEMATIC AFFINITY RULE. X. DEPENDENCE OF VALENCE ON TEMPERATURE. III, W. Biltz. Z. anorg. allgem. Chem. **109**, 132 (1919).

Discussion on dissociation of UO_3 from point of view of valence isobars.

713. ON THE ACIDS OF URANIUM, TUNGSTEN, AND MOLYBDENUM, G. F. Huttig. Z. angew. Chem. **35**, 391 (1922).

Discusses compn. curve of hydrated U oxides, particularly UO_3 and U_3O_8. Heat of formation for $UO_3.H_2O$ was obtained from calorimetric measurements of heat of neutralization: $UO_3 + H_2O(l) \rightarrow UO_3.H_2O\ (s) + 4.957$ kcal. Heat of formation for $UO_3.2H_2O$ is calculated to be $+7.428$ kcal.

714. THE THERMAL DECOMPOSITION OF SOME ACID PHOSPHATES AND SOME OXIDES, D. Balarev. Z. anorg. allgem. Chem. **134**, 75 (1924).

714—Continued

UO_3 (and other things) were studied with reference to effect of external pressure on temperature of decomposition. Decomposition temp. was found to vary with pressure for all of substances except UO_3. Decompn. was studied by means of temp.-time curves obtained when heat was applied at const. rate. Breaks in these curves indicated occurrence of endothermic reactions.

715. ON THE ORIGIN OF NORMAL URANATE IN THE HEATING OF UO_3 WITH METAL OXIDES, G. Tammann and W. Rosenthal. Z. anorg. allgem. Chem. **156**, 20 (1926).

Thermal decomposition of UO_3 begins at 600° and is complete at 865°C. Reaction product is first green and then black, forming U_3O_8 as end product. Table shows reactivity of UO_3 with metal oxides when heated at 600°,i.e., raised to that temp. twice in 10 min. and when equal molar amounts of powdered starting materials are used. Reactions usually result in evolution of heat and formation of uranates. No effect was found when UO_3 was heated with BeO, La_2O_3, CeO_2, and MoO_2.

Initial materials	Temp. at which reaction begins (°C.)	Color	
		Initial	Final
$Li_2CO_3 + UO_3$	380	Light yellow........	Yellowish orange.
$Ag_2O + UO_3$	150	Green...............	Brown.
$CaO + UO_3$	160	Light yellow........	Yellow.
$BaO + UO_3$	240	Light yellow........	Yellowish orange.
$SrO + UO_3$	125	Light yellow........	Orange.
$MgO + UO_3$	....	Light yellow........	Yellow.
$ZnO + UO_3$	200	Light yellow........	Yellow.
$CdO + UO_3$	425	Grayish yellow......	Orange yellow.
$HgO + UO_3$	175	Yellowish red.......	Orange yellow.
$CuO + UO_3$	340	Green...............	Brown.
$PbO + UO_3$	375	Light yellow........	Red.
$CoO + UO_3$	230	Green...............	Dark green.
$MnO + UO_3$	450	Yellowish green.....	Green.
$NiO + UO_3$	340	Yellowish green.....	Green.
$Al_2O_3 + UO_3$	450	Light yellow........	Yellow.
$Cr_2O_3 + UO_3$	230	Green...............	Green.
$Fe_2O_3 + UO_3$	....	Reddish brown.......	Brown.
$V_2O_3 + UO_3$	290	Light green.........	Green.

716. THE ACTIVITY OF VARIOUS METALS AND METAL OXIDE CATALYSTS IN PROMOTING THE OXIDATION OF METHANE BY AIR, W. P. Yant and C. O. Hawk. J. Am. Chem. Soc. **49**, 1454 (1927).

Investigation of catalytic effect of UO_3 on oxidation of methane in air. Efficiency of about 10.7%, or of same order as Pt black and Ni, was found. UO_3 was obtained at 325°C. ignition (4 hrs.) of $(NH_4)_2UO_4$.

717. SYSTEMATIC AFFINITY PRINCIPLES. XLVIII. THE HEATS OF FORMATION OF UCl_4, UCl_3, AND UO_3, W. Biltz and C. Fendius. Z. anorg. allgem. Chem. **176**, 49 (1928).

Heats of formation for chlorides were determined by indirect method from difference in heats of soln. of chlorides and of metal in 8N HCl. Ice calorimeter was used for calorimetric measurements. Heat of reaction for oxidation UCl_3 and UCl_4 to U^{+6} compound by soln. of $FeCl_3$ in HCl, or by soln. of ICl_3, compared with heat of solution of UO_3 in same media. Based on values obtained for heats of formation of UCl_3 and UCl_4, heat of formation of UO_3 is 294 cal. Comparison of results with those obtained for other metals shows that U is less noble than Fe and has about same affinity for Cl as has Th.

718. THE ENERGETIC STRUCTURE OF THE MOLECULE, G. Beck. Z. anorg. allgem. Chem. **182**, 332 (1929).

Discusses connection between thermochemical properties of UCl_4 and mol. structure of material, particularly as applied to amines. Total energy change of electronic rearrangement when UCl_4 is obtained from elements is 930 kcal. For UCl_3 value calculated as 824 kcal; for UO_3, 1020 kcal; and for UO_2, 695 kcal.

719. KINETICS OF REACTIONS BETWEEN COLLOIDS, V. A. Kargin. Zhur. Fiz. Khim. **1**, 691 (1930).

Similarly charged soln. of UO_3 and V_2O_5 react with each other forming colloidal complex $UO_3.2V_2O_5$. Spectrophotometric measurements of velocity of reaction indicate zero order with large period of induction. Reaction takes place between dissolved portions of colloidal acid, forming colloidal complex, rather than between particles.

720. KINETICS OF REACTIONS BETWEEN COLLOIDS. I-FORMATION OF URANIUM-VANADIUM COMPLEXES, V. A. Kargin. Z. anorg. allgem. Chem. **198**, 79 (1931).

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V_2O_5 soln. was prepd. by action of HCl on NH_4 vanadate and subsequent peptization of ppt. by washing with water. UO_3 soln. was similarly prepd. from NH_4OH and $UO_3(NO_3)_2$. Both soln. were purified by dialysis. Gradual addition of vanadium soln. to uranium soln. produces red coloration which passes into yellow upon heating; when sufficient vanadium has been added to bring comp. to proportion $UO_3.2V_2O_5$, addition of more vanadium gives red color, which is unchanged by heating. Absorption spectra and electrometric-titration curves show that $UO_3.2V_2O_5$ is definite complex distinct from original soln. Following formation $UO_3.2V_2O_5$ spectrophotometrically (at lambda 578 mu) showed that reaction has an induction period (2 to 4 hrs.), after which it is of zero order. If reaction took place between colloidal particles, concn.-time (c-t) curve would be exponential. Since c-t curve is linear, reaction takes place between those portions of two soln. that are in true soln.

721. ACTIVATED AND VAN DER WAALS ADSORPTION OF AMMONIA AND OF CERTAIN OTHER GASES, N. W. Taylor. J. Am. Chem. Soc. 53, 4458 (1931).

UO_3 appears to be a solid-solution of O in U_3O_8, and dissociation starting with $UO_{3.04}$ proceeds at 580° (15 min.) to $UO_{2.91}$ and hence to $UO_{2.84}$ (123 hrs.).

722. FUSED "ONIUM" SALTS AS ACIDS. I. REACTIONS IN FUSED AMMONIUM NITRATE, L. F. Audrieth and M. T. Schmidt. Proc. Natl. Acad. Sci. U.S. 20, 221 (1934).

UO_3 was found to react with fused NH_4NO_3 forming $UO_2(NO_3)_2$, NH_3, and H_2O.

723. HEATS OF FORMATION OF OXIDES AND OF SILICATES, A. I, Avgustinik. Zhur. Priklad. Khim. 20, 327 (1947).

Heats of formation of oxides plotted against atomic number of element show periodicity common to many other properties. Elements of 3rd and 5th group show characteristic peaks with lows for neighboring 4th group element; in 1st subgroup, values of heat of formation increase toward 7th group; in 2nd subgroups, they decrease. Halogens and metals of 1st subgroup occupy lowest points; "amplitude," i.e., spread between peak and lowest point, increases toward 7th group. From periodic chart of known heat of formation values, one can estimate unknown heat of formation of UO_3 to be 270 kcal/mole.

724. REPORT ON DETERMINATION OF DENSITIES OF SEVERAL URANIUM COMPOUNDS, H. F. Priest and G. L. Priest. MDDC-609, Aug. 10, 1942, declassified Jan. 3, 1947.

Values for apparent, or packing density, as well as absolute density have been determined for UO_3, UO_2. To determine packing density, material was ground to pass 120-mesh screen and known wt. placed in conical graduated tube which was capped. Tube was dropped a distance of 10 cm. in guiding tube onto a 1-in. rubber cushion. Packing was continued until there was no change in volume. Absolute density was determined using pycnometer with frequently checked alcohol as liquid (at 25°C). Results of two methods:

Material	Analysis (percent)	Absolute density 25°C	Packing density 27.5°C
UO_3	99.8	7.57 7.51 (average) 7.54	3.95
UO_2	99.34	10.26 10.29 (average) 10.28	4.96

725. A NEW PREPARATION OF URANIUM OXIDE (UO_3) AND A STUDY OF ITS DECOMPOSITION, A. Boulle and M. Domine-Berges. Compt. rend. **227**, 1365 (1948).

Very pure hydrated U oxide was obtained electrolytically from 10% solution of $UO_2(NO_3)_2$, by method described by Jolibois [Compt. rend. **215**, 319 (1942)]. It loses water, in air, at 380° to 390°C. At higher temps. UO_3 is transformed into U_3O_8. Reaction was studied with aid of thermobalance which showed 2-step loss of weight: 0.61% at 520° and 1.27% at 610°C. Existence of intermediary state, stable between these temps., was confirmed by simultaneously carried out thermal analysis which showed changes in structure at same temp. points; (UO_3 is amorphous, two other stages are crystalline). X-ray spectra, taken with CuK-alpha radiation, furnished further confirmation. Intermediate stage is best interpreted as solid solution corresponding to approximate composition $UO_{2.90}$.

726. METHOD OF PREPARING URANIUM TRIOXIDE, S. M. Fried, and N. R. Davidson. U. S. Patent No. 2,477,924, August 2, 1949, assigned to US AEC.

Process for preparation of UO_3 in crystalline form from amorphous U_3O_8. Accomplished by heating oxide between 450° and 750°C. under oxygen, pressures varying from 20 to 150 atmospheres. Time required for conversion varies from 12 to 112 hrs., depending upon pressures and temperatures. Time can be reduced to 1 1/2 hrs. by using O_2 pressures between 60 and 150 atmospheres at temperature from 700° to 750°C. Description of apparatus for preparation of UO_3 is given.

727. THE OXIDES OF URANIUM RESULTING FROM THE DECOMPOSITION OF URANYL OXALATE, A. Boulle, R. Jary, and M. Domine-Berges. Compt. rend. **230**, 300 (1950).

Experiments investigating decomposition of uranyl oxalate with and without vacuum, decomposition of uranyl oxalate by reduction, and reduction of UO_3 with CO are discussed. X-ray spectra of resulting U oxides compared. Explanation of mechanism decomposition of U oxalate is attempted.

728. DIELECTRIC PROPERTIES OF URANIUM OXIDES UO_2, U_3O_8, UO_3, M. Freymann and R. Freymann. Compt. rend. **230**, 2094 (1950).

Radiofrequency absorption measurements were made at temperatures ranging from plus 20° to minus 160°C and for frequencies: 1, 2, 5, 10, and 16 kc. Absorption is plotted as function of temperature for families of curves representing these frequencies. Results are: (1) UO_2 has zero absorption; (2) UO_3 shows strong absorption which decreases rapidly as temperature is lowered; (3) absorption curve for U_3O_8 goes through min. and then max. as temperature is lowered, which cannot be attributed to electronic origin. Further studies of U oxides, intermediate between UO_2 and UO_3 are in progress.

729. THE PREPARATION OF PURE OXIDES BY ELECTROLYSIS, M. Domine-Berges. Ann. chim. **5**, 106 (1950).

Electrolytic method of preparation of pure oxides and hydroxides described, based on Jolibois' theory of electrolysis of salt solns., according to which, and contrary to accepted views, pptn. of metal on cathode is secondary process, primary reaction being formation of hydroxide that in many cases is pptd. upon cathode. By using high voltages (up to 2000 volts), cathode can be surrounded by pure water; contamination of hydroxide by foreign ions is thus avoided,

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and product is obtained very pure. Through calcination hydroxide can be converted into one or several oxides, transformations from one oxide to next one being controlled by a thermogravimetric set-up. Among substances that are well adapted to this technique are U salts (nitrate and sulfate). Hydroxide obtained is $UO_3.H_2O$, which, upon calcination, yields UO_3 (amorphous), followed by a solid solution $UO_{2.90}$ (crystalline) then by U_3O_8 (crystalline); later presents two forms, one susceptible to a reversed process of reoxidation, other nonreoxidable [see Boulle and Domine-Berges, Compt. rend. **227**, 1365 (1948); ibid, **228**, 72 (1949)].

730. PREPARATION OF URANIUM TRIOXIDE, I. Sheft, S. Fried, and N. Davidson. J. Am. Chem. Soc. **72**, 2172 (1950).

Method for preparation of UO_3 described is considered to be superior to those commonly used because purity of product is dependent only on purity of original U_3O_8, which should be high for good results, and product is obtained in 100% yield. Oxygen is dried and purified during liquefaction so that this presents no problem, while U_3O_8 is generally obtained sufficiently pure. Within wide limits temperature at which reaction is run is not critical. Upper temperature limit, however, is important. Experiments made at 750°C. yielded oxides intermediate between U_3O_8 and UO_3. Even at 750°, however, UO_3 can be prepared by going to pressures over 400 psi. Preparations made at temperatures as low as 550° also yielded UO_3, but required somewhat longer time for complete reaction.

731. STUDIES ON THE URANIUM-OXYGEN SYSTEM. H. R. Hoekstra and J. J. Katz. AECD-2954, August 10, 1950, declassified Oct. 18, 1950.

U-O system is complicated by existance of multiplicity of crystalline forms and extensive regions of solid solution, with both reversible and irreversible decomposition regions. Discusses that portion of system extending from UO_3 down to UO_2. After reviewing conflicting phase relations found in literature, authors report some experimental studies on phase systems of O with Mg, Ca, Sr, and Ba diuranates and on thermal decomposition of crystalline phases of UO_3. Similarities between alkaline earth diuranates and U-O systems are shown, and some thermodynamic data on phase transformations are presented.

732. HIGHER OXIDES OF THE LANTHANIDE ELEMENTS. TERBIUM DIOXIDE, D. M. Gruen, W. C. Koehler, and J. J. Katz. J. Am. Chem. Soc. **73**, 1475 (1951).

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Investigation of comparative chemistry of lanthanide and actinide elements, atomic oxygen used to convert lower oxides of Pr, Tb, and U to PrO_2, TbO_2, and UO_3, respectively. No evidence for higher oxide formation has been obtained with Y, La, Nd, Sm, Eu, Gd, Yb, Hf, and Th.

6.1 Additional references not abstracted

"Beitrage zur Chemischen Kenntnis der Mineralkorper," M. H. Klaproth. Berlin, 1797, Vol. 2.

"Investigation of hydrofluoric acid and its most remarkable compounds," J. J. Berzelius. Ann. Physik Chem. (Pogg.) **1**, 1 (1824).

"Investigation of hydrofluoric acid and its most remarkable compounds," J. J. Berzelius. Ann. Physik Chem. (Pogg.) **2**, 113 (1824).

"On the properties of liquified hydrochloric acid gas," G. Gore. Phil. Mag. **29**, 541 (1865).

"On some properties of anhydrous liquified ammonia," G. Gore. Proc. Roy. Soc. (London) **A21**, 140 (1873).

"On several combinations with phosphorus perchloride," A. W. Cronander. Bull. soc. chim. France **19**, 499 (1873).

"On the specific volume of oxides," B. Brauner and J. I. Watts. Phil. Mag. **11**, 60 (1881).

"Hydrates of uranyl nitrate," M. deForcrand. Ann. chim. **3**, 5 (1915).

"Uranium colloids," S. I. D'yachkovskii and M. F. Ivanova. Zhur. Obshchei Khim. **5**, 638 (1935).

"Acetyl chloride as a chlorinating agent in inorganic chemistry," A. Chretien and G. Oechsel. Compt. rend. **206**, 254 (1938).

"Action of hydrogen chloride on titanium and uranium anhydride." G. P. Luchinskii, Zhur. Obshchei Khim. **10**, 769 (1940).

"The measurement and intrepretation of pH and conductance values of aqueous solutions of uranyl salts," D. A. MacInnes and L. G. Longsworth. MDDC-911, Nov. 24, 1942, declassified Mar. 5, 1947.

"The preparation of uranyl carbonate and measurement of its solubility," P. D. Miller, H. A. Pray and H. P. Munger. AECD-2740, Aug. 1, 1949, declassified Nov. 22, 1949.

7. Uranium Metal and Miscellaneous Reactions (800-809)

800. CRYSTAL STRUCTURE OF URANIUM, C. W. Jacob and B. E. Warren. J. Am. Chem. Soc. 59, 2588 (1937).

From x-ray powder photographs metallic U found to be orthorhombic with a:b:c: equal to 2.852 : 5.865 ; 4.945 (kX units), Z equal to 4 and density calculated at 18.97. Space group is V_h^{17} and atoms are in 3 equiv. positions on twofold axes Oy_4^1, with y equal to 0.105 ± .005. Structure is unique; may be considered as deformed hexagonal close-packed structure with 4 neighbors of each atom closer than other 8, indicating tendency to form 4 covalent bonds. Bond directions are not tetrahedral. Structure together with relatively high elect. resistance suggests that U is only pseudometallic.

801. CRYSTAL RADII OF THE HEAVY ELEMENTS, W. H. Zachariasen. Phys. Rev. 73, 1104 (1948).

Crystal radii for trivalent and tetravalent ions of heavy elements from Ac to Am as deduced from crystal structure data listed and briefly discussed.

802. CHEMISTRY OF THE HEAVY ELEMENTS, J. S. Anderson. Nature 163, 983 (1949).

Symposium organized by chem. division of Atomic Research Establishment, Harwell, on behalf of Chem. Soc., held at Rhodes House, Oxford, during March 28 to 30, 1949. One main topic of discussion was chemistry of heavy elements. First session of symposium was devoted to elements other than U. Second session, among others, discussed paper on lower oxides of U, which revealed complex system comparable with that of oxides of Mo and W, and a new and highly selective method for detection and determination of small quantities of U, based upon use of paper chromatography.

803. THE CHEMISTRY OF URANIUM. CHAPTERS 1 THROUGH 10, E. I. Rabinowitch and J. J. Katz. AECD-2624, declassified June 7, 1949.

Report is divided into chapters on nuclear properties of U; properties of U atom; U in nature; extraction of U from ores and preparation of U metal; physical properties of U metal; chem. properties of U metal; intermetallic compounds and alloy systems of U; U-H system; U borides, carbides, and silicides; and U compounds with elements of group V.

804. POSSIBLE F-SHELL COVALENCY IN THE ACTINIDE ELEMENTS, L. I. Katzin. Nature **166**, 605 (1950).

Arguments are presented to show that coordination of nitrate by uranyl ion is neither unique nor different in kind from that found lower in periodic table, and in particular in transition element such as cobalt.

805. THE REACTION BETWEEN URANIUM AND OXYGEN, D. Cubicciotti. J. Am. Chem. Soc. **74**, 1079 (1952).

Oxidation rate of uranium determined by measuring rate of metal's oxygen consumption in closed system over temperature range 90° to 240°C. Reaction rate followed parabolic oxidation law from 90° to 165°C. and linear law above 165°C. Considered unlikely that cause of transition from parabolic to linear is result of temperature rise. Evidence is cited for hypothesis that change in oxidation rate is caused by cracking in strained oxide film, strain being produced by increase in volume of oxide over that of metal consumed.

806. STUDIES OF RADIOACTIVE COMPOUNDS: I—VANDERBRANDEITE, I. H. Milne and E. W. Nuffield. Am. Mineral. **36**, 394 (1951).

Vandenbrandeite is triclinic with $a = 7.84$, $b = 5.43$, $c = 6.09$ (kX units); $\alpha = 91°52'$, $\beta = 102°00'$, $\gamma = 89°37'$ and cell content $2(CuUO_4.2H_2O)$. Angle table calculated and powder data given. Usual method of defining crystal systems in terms of crystallographic axes is inadequate; classification of crystals must rest on symmetry that has its origin in atomic arrangements. Review of rules for orienting triclinic crystals suggests that one important standardization is selection of conventional structural cell, which has as edges three shortest noncoplanar translations in lattice. This cell easily recognized from dimensions and angles regardless of setting, and is readily reoriented for special purpose. Preferred orientation of cell should, if possible, have α and β obtuse, and $a < b$. Should be designed to best describe mineral. Any noteworthy property, such as structural or morphological analogy to other minerals should influence choice of setting; in absence of outstanding feature morphological crystallographers will probably continue to designate some prominent direction within crystal as c-axis.

807. STUDIES OF RADIOACTIVE COMPOUNDS: II--META-ZEUNERITE, URANOPHANE, KASOLITE AND CUPROSKLODOWSKITE IN CANADA, D. D. Hogarth. Am. Mineral. **36**, 411 (1951).

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Meta-zeurerite, $CuO.2UO_3.As_2O_5.12H_2O$, occurs as small green plates in close proximity to sulphides, silver and altered pitchblende. Under microscope surfaces of plates show traces of 2 cleavages at right angles, Cu and U were determined by blowpipe and wet tests. X-ray powder pattern of mineral was identical with that of synthetic meta-zeunerite prepared in laboratory. First recorded occurrance in Canada of mineral. Uranophane, $CaU_2Si_2O_{11}.6H_2O$, occurs as clusters of radiating tiny yellow to greenish yellow needles and as yellow colloform crusts. Material may well be most common oxidation product of pitchblende in Canada. Was reported by Hoffman, G. C., Can. Geol. Surv. **12**, Ann. Report 16R, 1899, by Spence, H. S., Am. Mineral. **15**, 474 (1930), and by Palache, C. and Berman, H. Am. Mineral. **18**, 20 (1933). First occurrance identified by x-rays. Kasolite, $PbUSiO_6.nH_2O$, was noted as orange yellow crusts in association with an unidentified yellow-green radioactive mineral in fractures near center of radioactivity. Microscopic fragements show prismatic outline. Optically kasolite shows bluish interference color; main index of refraction above 1.78. Identification made by comparison of x-ray powder pattern with that of crystallized kasolite from Kasolo, Katanga. Mineral appears common in more highly radioactive areas in vein. Previously kasolite was known only from Kasolo, Belgian Congo. Cuprosklodowskite, $CuU_2Si_2O_{11}.6H_2O$, is one of the rarest of uranium oxidation products. Mineral was reported only by Vaes, J. P., Ann. Soc. Geol. Belgique **56**, Bull. B331 (1933) and by Novacek, R., Casopis Narodniho Musea, Praha **109**, 100 (1935). It occurs as tiny bright yellow-green needles in fissure in talcose argillaceous rock associated with other uranium minerals. Also seen close to sulphides and malachite on fine-grained carbonaceous rock as coating which under high magnification sometimes shows radiating fibrous structure, and it was noted on gum-like radioactive mineral.

808. STUDIES OF RADIOACTIVE COMPOUNDS: V-SODDYITE, D. H. Gorman. Am. Mineral. **37**, 386 (1952).

New observations on rare uranium silicate mineral soddyite. Formula $5UO_3.2SiO_2.6H_2O$ established as most plausible. New crystallographic data are recorded: orthorhombic, $a = 8.32$, $b = 11.21$, $c = 18.71$ A; space group-Fddd. Powder data presented agree with cell dimensions. Soddyite is optically negative, $2V = 84°$, $\alpha = 1.650$, $\beta = 1.685$, $\gamma = 1.712$, $X = c$, $Y = b$, $Z = a$,

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pleochroic, X colorless, Y very pale yellow, Z pale yellow-green; dispersion negligible, in disagreement with previous observations of r > v strong.

809. ON THE OXIDATION OF METALLIC URANIUM, J. Loriers. Compt. rend. 234, 91, (1952).

Oxidation of uranium in oxygen studied by differential thermal analysis from 100° to 360°C. Mechanism is similar to that of Ce oxidation. Initial homogeneous protective oxide layer thickens and breaks up in such a way that mass-time curve of oxidation changes from parabolic to linear type. Nature of oxides involved is discussed.

AUTHOR INDEX

APPENDIX

1. Listing of Publication Abbreviations

The following list gives the journal publication abbreviations used for this bibliography and the complete name of the publication.

Acta Chem. Scand.—Acta Chemica Scandinavica
Am. J. Sci.—American Journal of Science
Am. Mineral.—American Mineralogist
Anal. Chim. Acta—Analytica Chimica Acta
Ann.—Annalen der Chemie
Ann. chim.—Annales de chimie
Ann. chim. phys.—Annales de chimie et de physique
Ann. Physik Chem. (Pogg.)—Annalen der Physik und Chemie, (Poggendorf)
Arch. Pharm.—Archiv der Pharmazie
Arch. wiss. Kinde Russ.—Archiv fur wissenschaftliche Kunde von Russland.
Arkiv Kemi, Mineral. Geol.—Arkiv for Kemi, Mineralogi och Geologi
Ber.—Berichte der deutschen chemischen Gesellschaft
Ber. preuss. Akad. Wiss.—Berichte uber die zur Bekanntmachung Geeigneten Verhandlungen der kaiserlichen preussischen Akademie der Wissenschaften
Bull. classe sci., Acad. roy. Belgique—Bulletin de la classe des sciences, Academie royale de Belgique
Bull. soc. chim. France—Bulletin de la societe chimique de France
Bull. soc. imp. naturalistes Moscou—Bulletin de la societe imperiale des naturalistes de Moscou
Bull. soc. franc. mineral.—Bulletin de la societe francaise de mineralogie
Chem. News—The Chemical News and Journal of Physical Sciences
Compt. rend.—Comptes rendus hebdomadaires des seances de l'academie des sciences
Congr. avance. method. anal. spectrograph. produits met. (Paris)—Congres du groupement pour l'avancement des methodes d'analyse spectrographique des produits metallurgioues. (Paris)
Doklady Akad. Nauk S. S. S. R.—Doklady Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik
Gazz. chim. ital.—Gazzetta chimica italiana
Geol. Foren. i Stockholm Forh.—Geologiska Foreningens i Stockholm Forhandlingar

Handl. Svenska Vetenskapsaka.—Handlingar Kongliga Svenska Vetenskapsakademien
Helv. Chim. Acta—Helvetica Chimica Acta
Helv. Phys. Acta—Helvetica Physica Acta
Jahr. geol. Reich.—Jahrbuch der kaiserlich koniglich geologischen Reichsanstalt
J. Am. Chem. Soc.—The Journal of the American Chemical Society
J. Chem. Soc.—Journal of the Chemical Society
J. Chem. Soc. Japan—Journal of the Chemical Society of Japan
J. Indian Chem. Soc.—Journal of the Indian Chemical Society
J. prakt. Chem.—Journal fur praktische Chemie
J. Soc. Chem. Ind. (London)—Journal of the Society of Chemical Industry (London)
J. Wash. Acad. Sci.—Journal of the Washington Academy of Sciences
Nature—Nature (London)
Neues allgem. J. Chem.—Neues allgemeines Journal der Chemie.
Phil. Mag.—The Philosophical Magazine
Physik. Z.—Physikalische Zeitschrift
Proc. Natl. Acad. Sci. U. S.—Proceedings of the National Academy of Sciences of the United States of America
Proc. Roy. Sci. (London)—Proceedings of the Royal Society. (London). Series A. Mathematical and Physical Sciences; Series B, Biological Sciences
Quart. J. Sci.—Quarterly Journal of Science
Wiss. Veroffent. Siemens-Konzern—Wissenschaftliche Veroffentlichungen aus dem Siemens-Konzern
Z. anal. Chem.—Zeitschrift fur analytische Chemie
Z. ange. Chem.—Zeitschrift fur angewandte Chemie
Z. anorg. allgem. Chem.—Zeitschrift fur anorganische und allgemeine Chemie
Z. anorg. Chem.—Zeitschrift fur anorganische Chemie
Z. ges. Naturw.—Zeitschrift fur die gesamte Naturwissenschaft
Zhur. Fis. Khim.—Zhurnal Fizicheskoi Khimii
Zhur. Obshchei Khim.—Zhurnal Obshchei Khimii
Zhur. Priklad. Khim.—Zhurnal Prikladnoi Khimii
Zhur. Russ. Fiz. Khim. Obschestva—Zhurnal Russkogo Fiziko-Khimicheskogo Obschestva
Z. Metallkunde—Zeitschrift fur Metallkunde
Z. Naturforsch.—Zeitschrift fur Naturforschung
Z. physik. Chem.—Zeitschrift fur physikalische Chemie. Abteilung A. Chemische Thermodynamik, Kinetik, Elektrochemie, Eigenschaftslehre; Abteilung B. Chemie der Elementarprozesse, Aufbau der Materie

2. Listing of Numerical Reports

Reports of subcontractors and laboratories of the atomic energy research organizations of the United States and of foreign countries are assigned numerical reference numbers by the US AEC. This section lists the code and number and the abstract number of this bibliography of those reports (a) abstracted in the bibliography, (b) abstracted in the bibliography but which have later appeared in a technical journal or magazine, and (c) listed by title only in this bibliography.

(a) Abstracted in the Bibliography

MDDC-	Abst. No.
193	442
442	315
609	724
647	634
688	316
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1152	37
1242	322
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AECD-	Abst. No.
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Others	Abst. No.
AECU-1294	461
AERE-M/R-507	459
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BR-589	633
CEA-35	450
CEA-79	463
GS-C-74	332
NYOO-98	642
RMO-563	330
RMO-715	462

(b) Where it could be ascertained that an AEC report had been published in the open literature, the reference in this bibliography was given under that journal or publication designation and not under the AEC report number. The following reports are so designated in this bibliography:

Report	Abst. No.
MDDC-758	444
MDDC-1242	327
MDDC-1543	327
MDDC-1572	801

Report	Abst. No.
MDDC-1608	317
AECD-2139	39
NP-3208	805

(c) Listing of AEC Reports Given by Title Only

Report	Group	Report	Group
MDDC-279.....	U-oxides, general	MDDC-1729....	U-oxides, general
MDDC-366.....	U-oxides, general	AECD-1988....	U-oxides, general
MDDC-467.....	U-oxides, general	AECD-2307....	U-oxides, general
MDDC-901.....	U_3O_8	AECD-2740....	UO_3
MDDC-911.....	UO_3	AECD-2819....	U-oxides, general
MDDC-1564....	U_3O_8	NP-1602.......	U_3O_8

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