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

by S. M. Lang

National Bureau of Standards Circular 535
Issued January 9, 1953

For sale by the Superintendent of Documents, U. S. Government Printing Office
Washington 25, D. C. - Price 30 cents
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

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foreword</td>
<td>III</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Subject index</td>
<td>4</td>
</tr>
<tr>
<td>Bibliography</td>
<td>8</td>
</tr>
<tr>
<td>1. Reactions with uranium oxides</td>
<td>8</td>
</tr>
<tr>
<td>2. Uranium oxides, general</td>
<td>24</td>
</tr>
<tr>
<td>3. $\text{UO}_2$</td>
<td>37</td>
</tr>
<tr>
<td>4. $\text{U}_2\text{O}_5$</td>
<td>57</td>
</tr>
<tr>
<td>5. $\text{U}_3\text{O}_8$</td>
<td>59</td>
</tr>
<tr>
<td>6. $\text{UO}_3$</td>
<td>74</td>
</tr>
<tr>
<td>7. Uranium metal and miscellaneous reactions</td>
<td>84</td>
</tr>
<tr>
<td>Author index</td>
<td>88</td>
</tr>
<tr>
<td>Appendix</td>
<td>92</td>
</tr>
<tr>
<td>1. Listing of publication abbreviations</td>
<td>92</td>
</tr>
<tr>
<td>2. Listing of numerical reports</td>
<td>94</td>
</tr>
</tbody>
</table>
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 $\text{UO}_2$, $\text{U}_2\text{O}_5$, $\text{U}_3\text{O}_8$, and $\text{UO}_3$ 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 ($\text{UO}_2$). 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.

---

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 \( \text{UO}_2 \) and \( \text{U}_3\text{O}_8 \), 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; UO₂; U₂O₅; U₃O₈; UO₃; 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.
SUBJECT INDEX

1. Reactions With Uranium Oxides

1.1 Uranates, peruranates, and polyuranates:

<table>
<thead>
<tr>
<th>Compound</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂O</td>
<td>715</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>51, 715</td>
</tr>
<tr>
<td>BaO</td>
<td>1, 3, 4, 7, 9, 12, 17, 24, 25, 26, 36, 37, 38, 41, 49, 401, 628, 715</td>
</tr>
<tr>
<td>BeO</td>
<td>52, 715</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>12, 605, 628</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>16</td>
</tr>
<tr>
<td>CaO</td>
<td>4, 7, 9, 12, 17, 25, 26, 27, 28, 39, 40, 41, 45, 49, 416, 628, 715, 731</td>
</tr>
<tr>
<td>CdO</td>
<td>628, 715</td>
</tr>
<tr>
<td>CeO₂</td>
<td>32, 47, 50, 628, 715</td>
</tr>
<tr>
<td>CoO</td>
<td>31, 628, 715</td>
</tr>
<tr>
<td>CuO</td>
<td>27, 628, 715, 806</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>715</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>48</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>628, 715</td>
</tr>
<tr>
<td>HgO</td>
<td>715</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>21</td>
</tr>
<tr>
<td>K₂O</td>
<td>1, 4, 5, 6, 7, 8, 9, 10, 11, 12, 24, 26, 27, 33, 37, 606, 607, 628, 703</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>715</td>
</tr>
<tr>
<td>Li₂O</td>
<td>6, 7, 9, 12, 17, 628, 703, 715</td>
</tr>
<tr>
<td>MgO</td>
<td>7, 9, 12, 25, 30, 41, 49, 53, 54, 628, 715, 731</td>
</tr>
<tr>
<td>MnO</td>
<td>628, 715</td>
</tr>
<tr>
<td>MoO₂</td>
<td>628, 715</td>
</tr>
<tr>
<td>Na₂O</td>
<td>5, 6, 7, 9, 12, 13, 14, 15, 17, 19, 20, 21, 22, 26, 27, 42, 43, 303, 307, 309, 407, 409, 500, 616, 617, 628, 703</td>
</tr>
<tr>
<td>Nb₂O₃</td>
<td>16</td>
</tr>
<tr>
<td>NiO</td>
<td>628, 715</td>
</tr>
<tr>
<td>PbO</td>
<td>2, 4, 7, 17, 34, 401, 715</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>7, 9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>55, 808</td>
</tr>
<tr>
<td>SnO₂</td>
<td>628</td>
</tr>
<tr>
<td>SrO</td>
<td>4, 7, 9, 12, 25, 39, 41, 49, 715, 731</td>
</tr>
<tr>
<td>TiO₂</td>
<td>628</td>
</tr>
<tr>
<td>ThO₂</td>
<td>44</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>715</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>719, 720</td>
</tr>
<tr>
<td>ZnO</td>
<td>628, 715</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>46</td>
</tr>
<tr>
<td>General</td>
<td>18, 19</td>
</tr>
</tbody>
</table>

1.2 Complex uranates, peruranates, and polyuranates: 807

1.3 Additional references not abstracted (p. 23)
2. Uranium Oxides, General


2.2 Crystal structure: 317, 320, 430

2.3 Preparation: 311, 316, 318

2.4 Properties: 311, 315, 322, 323, 324, 326, 327, 615, 701

2.5 Reactions: 304, 307, 331, 333, 400, 401, 402, 442, 452, 627, 634, 805

2.6 Additional references not abstracted (p. 33)

3. UO₂

3.1 General: 9, 300, 301, 325, 328, 331, 421, 422, 445, 453, 458, 459, 469, 611, 628, 727


3.6 Additional references not abstracted (p. 55)
4. $\text{U}_2\text{O}_5$

4.1 General: 328, 331, 406, 407, 464, 500, 501, 605

4.2 Crystal structure: 317, 320, 447, 505

4.3 Preparation: 406, 407, 412, 413, 416, 447, 461, 468, 500, 502, 503, 605, 705

4.4 Properties: 447, 500, 503, 504

4.5 Reactions: 731

4.6 Additional references not abstracted (p. 58)

5. $\text{U}_3\text{O}_8$

5.1 General: 9, 325, 328, 500, 501, 615, 630, 639, 642, 713, 727


5.6 Additional references not abstracted (p. 72)

6. $\text{UO}_3$

6.1 General: 304, 325, 326, 331, 703, 712, 713, 721

6.2 Crystal structure: 308, 317, 320, 430, 462, 633, 636, 721, 725

6.4 Properties: 315, 322, 323, 324, 326, 327, 425, 444, 446, 448, 456, 462, 619, 627, 702, 708, 717, 718, 723, 724, 728


6.6 Additional references not abstracted (p. 83)

7. Uranium Metal and Miscellaneous Reactions

444, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809

8. Other Uranium Oxides

8.1 UO$_2$: 304, 308, 310, 315, 316, 335, 448, 450, 454, 500

8.2 U$_2$O$_7$: 407

8.3 U$_3$O$_7$: 464

8.4 U$_4$O$_{10}$: 416

8.5 U$_7$O$_{20}$: 305

8.6 Uranium Red: 17, 24, 26, 28, 303, 305, 407, 414, 456, 504
BIBLIOGRAPHY

1. Reactions With Uranium Oxides

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


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.


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


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


When $K_2U_2O_7$ is reduced in hydrogen, material becomes violet-black but shom 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 $NH_3$.


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
5—Continued

$\text{Na}_2\text{O}.2\text{UO}_3.6\text{H}_2\text{O}$. Ignition of hexahydrate produces anhydrous salt. $\text{K}_2\text{U}_2\text{O}_7$ can be pptd. from uranyl salt soln. with excess KOH, orange-yellow ppt. when dried in air is reported to have composition $\text{K}_2\text{O}.2\text{UO}_3.6\text{H}_2\text{O}$.


Crystalline $\text{Na}_2\text{O}.2\text{UO}_3$ is prepared by dissolving $\text{UO}_2\text{Cl}_2$, $\text{NaCl}$, and $\text{NH}_4\text{Cl}$ in water, evaporating aqueous soln. and igniting residue. Material obtained is orange-yellow rhombic crystalline material, apparently isomorphous with corresponding $\text{K}$ compound and with $\text{Li}_2\text{UO}_4$. Decomposes when ignited at white heat and completely reduced to $\text{UO}_2$ 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 $\text{K}_2\text{U}_2\text{O}_7$, fresh $\text{UO}_2\text{Cl}_2$ is mixed with $\text{KCl}$ and dissolved in water, evaporated to dryness. Residue is freed of $\text{NH}_4\text{Cl}$ 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 $100^\circ\text{C}$., 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 $\text{UO}_2$ is incomplete. Insol. in water and easily sol. in acids. $\text{Li}_2\text{UO}_4$ can be prepared in the same manner. Properties of lithium uranate are discussed particularly as regards its stability in relationship to the $\text{K}$ and $\text{Na}$ 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.


Crust of $\text{Na}_2\text{UO}_4$ is formed on surface of melt of $\text{U}_3\text{O}_8$ and $\text{NaCl}$ upon fusion in Pt crucible. Purification can be carried out by cooling and leaching with cold water. $\text{Na}_2\text{CO}_3$ is also valuable in the preparation. Brilliant green to golden-yellow flakes are obtained which are insol. in water, slightly sol. in dil. acids.
Continued

yield a yellow soln., and do not melt at bright-red heat. $\text{K}_2\text{U}_2\text{O}_4$ can be prepared in same manner, as greenish-yellow flakes which fuse at bright-red heat. They are optically negative and insol. in water. $\text{Li}_2\text{U}_2\text{O}_4$ has approximately same properties as $\text{Na}_2\text{U}_2\text{O}_4$ and is prepared in same manner. $\text{Ca}_2\text{U}_2\text{O}_7$ can be obtained very slowly by melting $\text{U}_3\text{O}_8$ with $\text{CaCl}_2$. Forms as small crystalline crust which can be separated from $\text{CaCl}_2$ by extraction with water. When pure, it is in form of yellow flakes. $\text{Ca}_2\text{U}_2\text{O}_7$ can be prepared by heating $\text{U}_3\text{O}_8$ with $\text{Ca(ClO}_3)_2$and $\text{NaCl}$ or $\text{CaCl}_2$. Material is formed as yellow-green flakes which are insol. in water but sol. in dil. acids. $\text{Ba}_2\text{U}_2\text{O}_7$ can be obtained in crystalline form by heating $\text{U}_3\text{O}_8$ with $\text{Ba(ClO}_3)_2$ similar to the preparation of the Ca salt. Crystallization is much faster. $\text{BaUO}_4$ 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 $\text{SrUO}_4$ and $\text{SrO}_2\text{UO}_4$ are reported similar to Ca salts. $\text{RbUO}_4$ is obtained in same manner as sodium salt and has approximately same property. $\text{MgUO}_4$ is obtained by melting $\text{U}_3\text{O}_8$ with $\text{MgCl}_2$ or by heating with chlorate and adding $\text{MgCl}_2$. 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).

$\text{K}_2\text{UO}_4$ prepared from uranyl phosphate by heating for several hours with KOH and excess $\text{K}_2\text{SO}_4$ between temperature of formation of $\text{KUO}_2\text{PO}_4$ and $\text{UO}_3$. 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.


Continuation of earlier work by author. Valuable early data on $\text{UO}_2$ and $\text{U}_3\text{O}_8$, 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).

$\text{KUO}_2\text{PO}_4$ prepared by heating $(\text{UO}_2)(\text{PO}_4)_2$ with excess $\text{K}_2\text{SO}_4$ and $\text{K}_2\text{O}$. Double phosphate decomposes in presence of alkali forming...
10—Continued

\( K_2\text{UO}_4 \). \( K_2\text{UO}_4 \) prepared from uranyl phosphate by heating for several hours with excess \( K_2\text{SO}_4 \) between temperature of formation of potassium uranyl phosphate and \( \text{UO}_3 \). Consists of fine orange-yellow flakes which appear hexagonal under microscope.


Double phosphate, \( K\text{UO}_2\text{PO}_4 \), when combined with alkali, forms the uranate, \( K_2\text{UO}_4 \). Uranate is usually contaminated with other reaction products. Consists of fine orange-yellow flakes.


\( K_2\text{U}_2\text{O}_7 \) can be obtained from uranic acid mixed with \( \text{KCl} \) and ignited strongly for two hours. Melt which becomes a grayish-brown gradually changes to orange-yellow, then boiled with water and dried. \( \text{Li}_2\text{UO}_4 \) can be prepared in the same manner as \( K_2\text{UO}_4 \). \( \text{Na}_2\text{U}_2\text{O}_7 \) prepared by igniting mixture of pptd. uranic acid and \( \text{NaCl} \) for two hours in blast lamp, boiling residue with water to leach out impurities, drying at 100°C. \( \text{BaU}_2\text{O}_7 \) obtained by short intense heating of uranic acid with \( \text{BaCl}_2 \). Purification is similar to that for \( K_2\text{U}_2\text{O}_7 \). Crystallization of \( \text{MgUO}_4 \) reported with brown, irregular and amorphous materials being obtained. \( \text{CaU}_2\text{O}_4 \) obtained by heating uranic acid with \( \text{CaCl}_2 \). Crystallization of \( \text{SrU}_2\text{O}_7 \) is analogous to corresponding \( \text{Ca} \) salt; however, proceeds at slower rate. When freshly pptd. uranic acid is heated to dull-red heat with slight excess \( \text{BiCl}_3 \), silky brick-red crystals of composition \( 2\text{Bi}_2\text{O}_3\text{.3UO}_3 \) or \( (\text{BiO})_4\text{U}_3\text{O}_{11} \) are formed. Excess \( \text{BiCl}_2 \) is volatilized by prolonged heating.


\( \text{Na}_2\text{UO}_4 \) prepared by decomposition of uranium molybdate with \( \text{NaCl} \) is in form of brilliant, reddish-yellow, transparent, rhombic prisms which are strongly birefringent.


\( \text{Na}_2\text{O}_2\text{.2UO}_3 \) can be obtained by prolonged boiling of a yellow soln. of \( \text{Na}_4\text{UO}_5\cdot\text{H}_2\text{O} \).
15. ON SODIUM PEROXIDE, T. Poleck. Ber. 27, 1051 (1894).

Na₂O₂₂UO₃ can be obtained by prolonged boiling of a yellow soln. of Na₄U₂O₇.₅H₂O.

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 3UO₃.₅B₂O₅.


Structure of peruranates is discussed and peroxide formula H₂U₂O₁₀ = R₂O₂.₂UO₄ and R₄UO₆ = 2R₂O₂.₄UO₄ is proposed. Preferred since substances can be characterized as compounds of metallic peroxides with UO₄.₄Na₂UO₆ obtained by dissolving hydrated UO₄ in excess NaOH and adding H₂O₂. 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 Li₄UO₆ was obtained, but material is very unstable, losing oxygen when allow to stand over sulfuric acid. BaU₂O₆.₅H₂O 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 CO₂. BaUO₃.₈H₂O is obtained in the same manner as corresponding Na salt, using BaCl₂. Orange, powderlike crystals result after drying ppt. over sulfuric acid and soda lime. Dark-orange lead peruranate, Pb₃U₂O₁₀, is obtained by mixing soln. of Na₂U₂O₇ 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 H₂O₂. Calcium peruranate, Ca₄UO₈.₁OH₂O, is formed as ppt. of pale-yellow crystals by decomposition of the corresponding soda salt with CaCl₂. Crystals decompose with sulfuric acid by separating H₂O₂.


Structure of peruranates is discussed and proposed that peroxide formula R₂U₂O₁₀ = R₂O₂.₂UO₄ and R₄UO₆ = 2R₂O₂.₄UO₄ is preferred since substances can be characterized as compounds of metallic peroxides with UO₄. See also Bull. soc. chim. France 22, 8 (1899).

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

\[
\begin{array}{c}
\text{NaO} \\ \\
\text{NaO-O-U=O} \\ \\
\text{Na}_2\text{O}_2
\end{array}
\]

assigned to \(\text{Na}_4\text{UO}_8\).


Heat of reaction for \(\text{UO}_3\cdot\text{H}_2\text{O} + \text{H}_2\text{O} = \text{UO}_4\cdot2\text{H}_2\text{O}\) calculated as -6151 cal. \(\text{Na}_4\text{UO}_8\) crystallizes with 9 molecules water. \(\text{UO}_3\cdot\frac{3}{2}\text{H}_2\text{O}\), or \(\text{H}_2\text{U}_2\text{O}_7\), is formed somewhat above 160°C. at water-vapor pressure of 15 mm Hg. At 300°C. goes to anhydrous \(\text{UO}_3\). Heat of neutralization for one mole of material by 2 moles of \(\text{NaOH}\) is +17.859 kcal. Heat of reaction liberated in decomposition of \(\text{Na}_2\text{UO}_8\) with sulfuric acid is 36,497 cal.


Indium uranate can be prepared by pptn., using soln. of In chloride with \(\text{Na}_2\text{UO}_4\).


Investigation to determine whether product obtained in analysis of \(\text{U}\) by Patera's method was correctly represented by formula \(\text{NaO(\text{U}_2\text{O}_3)}_2\). 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 \(\text{Na}_4\text{U}_5\text{O}_{17}\). For Patera's ppt. formula was \(\text{Na}_4\text{U}_4\text{O}_{35}\). While Na uranate may actually be pptd. as \(\text{Na}_2\text{U}_2\text{O}_7\), 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.


Uranates of type \(\text{R}_2\text{UO}_4\), diuranates of type \(\text{R}_4\text{U}_2\text{O}_7\), and peruranates of type \(\text{R}_2\text{UO}_8\) 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 pyrocious, of P, Sh, and Bi in higher condition of oxidation.


$\text{UO}_2\text{Cl}_2$ is reduced by hydrogen with heat to $\text{UO}_2$ and HCl. Crystals heated in open tube with an excess of KOH form red peruranate, $\text{K}_2\text{UO}_5$, which slowly loses oxygen, giving $\text{K}_2\text{UO}_4$. Yellow $\text{BaUO}_4$ is pptd. from $\text{UO}_2\text{Cl}_2$ by $\text{BaCl}_2$.


$\text{UO}_2\text{Cl}_2$ in dil. soln. was treated with $\text{BaCl}_2$, $\text{SrCl}_2$, $\text{CaCl}_2$, or $\text{MgCl}_2$ in sol. before adding NH$_4$OH free from carbon. Uranates were pptd. as the hydrates. They can then be dried to anhydrous salts.


Uranates, in general, correspond to formula $\text{R}_2\text{UO}_4$. When $\text{UO}_2\text{Cl}_2$ was fused with KOH in presence of O$_2$, $\text{K}_2\text{UO}_5$ was obtained. Heated to fusion with KOH, O$_2$ was evolved and $\text{K}_2\text{UO}_4$ remained. Pure $\text{K}_2\text{UO}_5$, $\text{Na}_2\text{UO}_5$, and $\text{BaUO}_4$ were prepared and analyzed. $\text{CaUO}_5$ was obtained, impure, with $\text{CaUO}_4$. Salts vary in color from red to orange and yellow.


K and Na react with $\text{UO}_2\text{Cl}_2$ to give $\text{UO}_2$ contaminated with alkali uranate; Mg and Al react to give $\text{UO}_2$. $\text{CaO}$ and $\text{Ba(OH)}_2$ react with $\text{UO}_2\text{Cl}_2$ to give $\text{UO}_2$; $\text{CaO}$ reacts to give $\text{UO}_2$ with a small amount of copper uranate.


$\text{Na}_2\text{O}.2\text{UO}_3$ obtained when Et$_2$O soln. of $\text{UO}_2(\text{NO}_3)_2$ treated with metallic Na. Decomposition of $\text{UO}_2(\text{NO}_3)_2.3\text{H}_2\text{O}$ yields orange-red $\text{UO}_3$, which is formed at 250° to 300° C. $\text{CaO}.2\text{UO}_3$ was formed using $\text{CaO}$. Impossible to ppt. anhydrous $\text{UO}_2(\text{NO}_3)_2$ from soln. of AmOH.

Dissertation includes considerable information on properties of 
peruranates; colors: $R_2L_2O_10$, 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 $H_4UO_8$ 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 BARE 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 
18, 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 
$UO_2SO_4.31/2H_2O$ 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 ppts. from $Ce$ salts by $NH_4OH$, 
reddish-brown flakes of $U(OH)_4$ are ppts. 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 
have same composition, other than water content, as blue oxide ob-
tained 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, 
$Ce^{4+}-Ce^{4+}U^{4+}=Ce^{3+}-Ce^{3+}O_6U^{4+}$.

33. ACTION OF ULTRAVIOLET RAYS ON MINERAL COMPOUNDS. SECOND 
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.


Impure uranium hyponitrite was prepared by treating uranium nitrate soln., cooled in ice salt bath, with 5% Mg amalgam. Yellow $\text{PbU}_2\text{O}_7$ was obtained by treating soln. with $\text{Pb(NO}_3)_2$.


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

$$O_2^-=U^{2+}(O_R^2)^2$$

thought probable for peruranates.


Tabular golden-yellow single crystals of $\text{BaUO}_4$ were prepared by fusion of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ in 8-fold excess of $\text{BaCl}_2$. 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 $a = 5.751$, $b = 8.135$, $c = 8.236$ Å, all $\pm 0.005$ Å, 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.


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.


$U$ 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 $U^{VI}$ ion must be too large to allow stable tetrahedra grouping of $O$ ions. Assumptions tested on $BaUO_4$ (was proposed to use $BeU_2O_7$). Complete lattice determination was made, confirming predicted absence of $UO_4$ groups. Structure should account for nonsolubility of uranates.


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.


Preparation of alkaline earth polyuranates is critically discussed. Thermal decomposition of double alkaline earth uranyl acetates provides simplest approach to synthesis of compounds. MgU$_2$O$_7$ 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.


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$_2$UO$_6$, Na$_4$UO$_8$, and Na$_2$U$_2$O$_{10}$, effect of absorption by Na$_4$UO$_2$(CO$_3$)$_3$ being relatively unimportant.


Chemical and x-ray diffraction analyses and interpretation of pH and conductivity data indicate that two uranates, Na$_2$U$_7$O$_{22}$ and Na$_4$U$_7$O$_{24}$ (or mixtures thereof) are obtained in the pptn. of uranate with NaOH from UO$_2$(NO$_3$)$_2$ soln.


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


System was investigated in temperature range from 1650° to 2300° C, eutectic temperature is 2080°±20° C at about 45 mole % UO₂ and 55 mole % CaO. CaO takes no detectable amount of UO₂ into solid-solution, but UO₂ 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: Ca₂UO₄ (2CaO·UO₂), tetragonal double oxide of unknown structure; and CaUO₃ (CaO·UO₂), cubic, a = 10.727±0.002 kX. Structure of latter is equivalent to Type-C rare-earth oxide structure, with Ca²⁺+U⁴⁺ replacing 2M³⁺. Compound CaUO₃ is completely indexed in terms of rare-earth Type-C structure, and partially indexed in terms of fluorite cell, containing 16 molecules CaUO₃ per unit cell. Compound Ca₂UO₄, 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 Ca₂UO₄ in conformity with Zachariasen's data for spatial requirements of Ca²⁺, O²⁻, and U⁴⁺.


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. UO₂ solid-solution is cubic, extending from 0 to 40% ZrO₂ by weight, lattice parameter varies from 5.460 to 5.277 kX with increasing ZrO₂. ZrO₂ solid-solution is tetragonal, extending from 50 to 100% ZrO₂, lattice parameters vary: a₀ from 5.23 to 5.07 kX and c₀ from 5.27 to 5.16 kX. Evidence of a solid-solution in monoclinic ZrO₂.

47—Continued

Dark-blue cubic crystals of cerium uranium oxide obtained by Hoffman et al. [Ber. 48, 20 (1915)] were considered definite chemical compound $2\text{CeO}_2\cdot\text{UO}_2$. 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, $(\text{Ce}, \text{U})_2\text{O}_3$, of fluorite-type lattice.


Fluorite phase was observed between 27.0 and 66.7 mole % Er$_2$O$_3$, lattice constant varied linearly from $5.349 \pm 0.001$ to $5.303 \pm 0.001$ Å 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 $\text{U}_3\text{O}_8$ and Er$_2$O$_3$ are given by extrapolated lattice constants.


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 diurate-oxygen systems found to be reversible below 1100°. Equilibria dissociation pressures of oxygen so obtained permit outlining biphasic 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 $\text{Me}_2U_2O_6$ indicate structural similarity to uranium dioxide.

Magnesium diuranate consists of two solid phases, $\text{MgUO}_4$ and $\text{Mg}_3\text{U}_3\text{O}_{10}$. Samples in magnesium diuranate system with the empirical formulas $\text{Mg}_2\text{U}_2\text{O}_{6.04}$ and $\text{Mg}_2\text{U}_2\text{O}_{5.90}$ 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). $\text{Mg}_2\text{U}_2\text{O}_6$ structure interpreted 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 $\text{UO}_2$. Calcium and strontium compounds having formula $\text{MU}_2\text{O}_6$ also exhibit fluorite structure with unit cell size increasing with size of alkaline earth atom, i.e., $\text{CaU}_2\text{O}_6$, 5.379 A, and $\text{SrU}_2\text{O}_6$, 5.452 A. Densities of solids calculated from X-ray data are: $\text{Mg}_2\text{U}_2\text{O}_6$, 8.97 g/cm$^3$; $\text{CaU}_2\text{O}_6$, 8.71 g/cm$^3$; and $\text{SrU}_2\text{O}_6$, 9.07 g/cm$^3$.


Series of pure $\text{CeO}_2$-$\text{UO}_2$ mixed crystals prepared by igniting Ce(IV) and U(IV) salts at 1200°C in high vacuum, all crystals were blue. Specific resistance of $\text{UO}_2$, $5 \times 10^3$ ohm-cm, decreased with $\text{CeO}_2$ additions to minimum of $2.5 \times 10^2$ ohm-cm at 40 mole % $\text{CeO}_2$. High conductivity is explained by electron exchange between valence states. Contrast is drawn with behavior of brown $\text{UO}_2$-$\text{ThO}_2$ mixed crystal series.

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 UO₂. Binary eutectic may be at about 20 mole % UO₂ and about 1800°±50°C (from visual observation of heated X-ray samples).


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 UO₂.


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 4UO₂:1MgO (about 96 wt. % UO₂) to mole ratio 1UO₂:50MgO (about 12 wt. % UO₂).


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 U₃O₈ decomposes to a lower oxide, eventually to UO₂.
THE EQUILIBRIA OF PARTIAL BINARY SYSTEMS OF UO₂ WITH
Al₂O₃, BeO, MgO, and SiO₂. PART IV—THE SYSTEM
UO₂-SiO₂, S. M. Lang, C. L. Fillmore, and R. S. Both, M&NS
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 com-
pounds, solid-solubilities, nor any other solid-state reactions
present at temperatures from 800°C to 1600°C within the composi-
tional range from 10 to 90 mole % UO₂. Binary eutectic may be at
approx. 1600°C ± 50°C (from visual observations of heated X-ray sam-
ples).

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.

"On the composition of a group of uranium silicate minerals," R.

"On the composition of a group of uranium silicate minerals," R.

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

"Zur Kenntnis der Peruransaure und Peruranate," H. Daehr. Ber-
lin, 1928.

21, 1506 (1938).
2. Uranium Oxides, General (300-336)


Reports first preparation of $\text{UO}_2$ although at that time was believed to be element rather than oxide. $\text{UO}_2$ was prepared by reduction of $\text{UO}_3$ in a C crucible. Method of analysis (for $\text{UO}_2$) is given.

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

Identification of $\text{UO}_2$ (as prepared by Klaproth) as oxide and not metal as assumed.


Ammonium uranium red obtained as blood-red ppt. from uranyl soln. when treated with $(\text{NH}_4)_2\text{S}$ and reaction mixture allowed to stand in presence of air for from one to two days. Substance can be dissolved in acids, evolving $\text{H}_2\text{S}$ and free $\text{S}$. $\text{NH}_3$ can be displaced by other bases upon boiling with alkali or alkaline earth hydroxide. Sodium uranium red can be pptd. from uranyl soln. using $\text{H}_2\text{S}$ and $\text{NaOH}$; no further investigation was made. Potassium uranium red is obtained from ammonium uranium red by boiling with KOH solution.


Uranium red consists of mixture of uranyl hydroxide with red modification of $\text{UO}_2\text{S}$. Ammonium U red obtained as blood-red ppt. from uranyl salt soln. when treated with $(\text{NH}_4)_2\text{S}$ 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).


Anhydrous peroxide, $\text{UO}_4$, obtained when mixture of $\text{H}_2\text{O}_2$ and uranyl nitrate was treated with great excesses $\text{H}_2\text{SO}_4$ and allowed to stand for long time. Unsuccessful attempts to prepare $\text{UO}_4$ by strong oxidation of acidic, neutral, or alk. soln. of
uranic acid and uranates reported. $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ can be formed as a yellowish-white ppt. when pure dil. $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}$ or $\text{O}_2$. When $\text{H}_2\text{O}_2$ is used in excess, $\text{O}_2$ is lost during filtration, especially when mother liquor is still warm. Formula for $\text{UO}_4$, although it forms wide variety of peruranates, is proposed to be $2\text{UO}_3 \cdot \text{UO}_6 \cdot 6\text{H}_2\text{O}$. These peruranates can be regarded as salts of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$; however, in view of behavior with alk., are usually formulated as triple molecules, in which one or more $\text{UO}_3$ groups may be replaced by an alkali. Peroxide formula showing that type of linkage for peruranates is proposed.


Discussion. If pptn. of U from soln. using carbonate-free ($\text{NH}_4$)$_2$S. Pptn. beaker must be kept at 100°C until soln. is clear. Same results are obtained using $\text{NH}_4\text{OH}$. Potassium uranium red can be prep’d quickly by treating U salt soln. with freshly prep’d 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 $2\text{UO}_3 \cdot \text{UO}_2 (\text{OK}) \cdot \text{SK}$ for K red. Ammonium uranium red can be obtained as blood-red ppt. from uranyl salt soln. when treated with ($\text{NH}_4$)$_2$S and reaction mixture allowed to stand in presence of air for from one to two days. Compound $\text{U}_7\text{O}_{20}$ was prep’d by conversion of uranyl sulfide to oxyacid. Material is black.


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.


Large number of peroxides, including $\text{UO}_4$ and double peroxides of U with $\text{Ba}$, $\text{Na}$, and $\text{Li}$ are mentioned. Peroxides of U and Mo are compared and structures for $\text{UO}_3$ and $\text{UO}_4$ 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.


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 KRISTALL-STRUKTUREN, (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
such glasses (including a red which is insensitive to temperature) are given.


Prepn. and properties of some U compounds important in toxicological work are given, including $\text{UO}_3$, $\text{UO}_4$, and $\text{U}_3\text{O}_8$. See also: "Pharmacology and Toxicology of Uranium Compounds," Voegtlin and Hodge, McGraw-Hill Book Co., New York, 1949, Chapter 1.


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 appendices on absorption and fluorescence wavelengths, special preparations. Preparation and investigations of absorption spectrum (a), fluorescent spectrum (f), temperature effect (t), and isotopic substitution effect (i) on a great number of hydrated $\text{UO}_2$ and $\text{UO}_4$ compounds of nitrates, sulfates, halides, and some selenides. Bondstrengths, lengths, and crystal structure for U and uranyl compounds are also discussed.


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$_2$C$_3$ 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$_2$N$_3$ is body-centered cubic, $a = 10.678$, and has Mn$_2$O$_3$ 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
317—Continued

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$_2$O$_5$ is orthorhombic, a = 6.72, b = 31.8, c = 8.27. Structure is related to U$_3$O$_8$ and UO$_3$. One phase region exists from U$_2$O$_5$ to UO$_3$ in which various structures continuously transform from one to another. Note: All lattice constants are given in kX units.


Procedure is given for purification of U oxide by converting to nitrate and partitioning nitrate between large amount of Et$_2$O and relatively small amount of H$_2$O. 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$_3$O$_6$.


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$_2$ and U$_2$O$_5$, two phases, one is UO$_{2.8}$ with disordered fluorite structure, other is U$_2$O$_5$, orthorhombic, closely related to U$_3$O$_6$ in structure; (5) between U$_2$O$_5$ and U$_3$O$_8$, one phase, structure changing continuously with composition; and (6) above U$_3$O$_8$, only individual oxides examined, but structure of UO$_3$ very similar to that of U$_3$O$_8$. Evidence that single phases of intermediate character can be produced.
Structure of $\text{LO}$, $\text{UO}_2$, $\text{U}_2\text{O}_5$, and $\text{U}_3\text{O}_8$ are described. Summarizes material reported on U oxides presented in earlier reports.


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.


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 $1, 10^{-3}, \text{and } 10^{-6}$ atmospheres. See abst. no's. 323 and 327.


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


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
324—Continued

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.


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 prep. 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.


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


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
oxide in hot concentrated $\text{H}_2\text{SO}_4$, 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.


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 $\text{U}_3\text{O}_8$ 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.


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.


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-O-$\text{H}_2\text{O}$ 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.


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


Liq. NO₂ reacts with U oxides at 25°C and 1.2 atmospheres to form uranyl nitrates containing varying quantities of NO₂. Anhydrous oxides, such as UO₃ and U₃O₈, react slowly and only partially to yield (the nitrate). UO₃ and UO₄ dihydrates react rapidly and completely, also monohydrate of UO₃. All NO₂-containing uranyl nitrates are sensitive to H₂O and lose NO₂ readily on contact with moist air.


Brief summary of methods described in literature for refining U oxides and producing uranium metal from UO₂ is given. Actual process used for Kjeller pile (first Norwegian reactor) is not discussed.


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.


Yellow ppt. obtained by reaction of H₂O₂ with aqueous UO₂(NO₃)₂ has been given formulas UO₄·3H₂O, UO₈(UO₂)₂6H₂O, UO₃·H₂O₂·H₂O, etc. Experiments using various investigative methods resulted in conclusion that substance is (UO₂)₂UO₈·9H₂O at ordinary temperatures; three H₂O molecules being lost between 90° and 120°C, and additional O₂ and H₂O being lost at an unspecified higher temperature.
2.1 Additional references not abstracted


"Further observations respecting the decomposition of the earths, and other experiments made by burning a highly compressed mixture of gaseous constituents of water," E. D. Clarke. Ann. Physik (Gilbert) 62, 337 (1819).


"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).


2.1—Continued


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


2.1—Continued


"Chemical research—analytical." J. I. Watters, M. Fred, S. Shell, I. Corvin, and W. Byerly. AECD-1988, May 12, 1945,
2.1—Continued

declassified May 18, 1948. (Concerning determination of oxygen in uranium by vacuum fusion.)


3. \( \text{UO}_2 \) (400-469)

400. \textbf{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 \( \text{UO}_2(\text{NO}_3)_2 \) in water and EtOH are reported. Prepn. of \( \text{UO}_2 \) by reduction of higher U oxides is discussed.


Reduction of higher oxides of uranium to \( \text{UO}_2 \) using hydrogen as opposed to earlier method which used carbon. Crystals are ordinarily micro. octahedra; however, form will vary considerably with method of preparation. \( \text{UO}_2 \) can also be obtained by reduction of \( \text{KUO}_2\text{Cl}_3 \) with dry hydrogen as long as HCl is evolved. Residue is leached with water and dried. \( \text{UO}_2 \) obtained is stable in air, goes to \( \text{U}_3\text{O}_8 \) when heated (with swelling) and is insol. in HCl and H\(_2\)SO\(_4\). Study of atomic weight of uranium is reported. BaO.2\( \text{UO}_3 \) obtained by pptn. from boiling soln. of \( \text{UO}_2\text{Cl}_2 \) 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.2\( \text{UO}_3 \) prepared from solutions of \( \text{UO}_2(\text{NO}_3)_2 \) 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 \( \text{U}_3\text{O}_8 \).

402. \textbf{CONTRIBUTIONS TOWARD THE HISTORY OF URANIUM, L. R. Lecanu. J. min. sci. accessories 11, 279 (1825).}

Discuss . . reduction of higher oxides of U to \( \text{UO}_2 \) using H\(_2\) as opposed to C.

403. \textbf{RELATIVE STUDIES ON THE ACTION OF WATER VAPOR AT HIGH TEMPERATURE ON METALS. II 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 \( \text{UO}_2 \), \( \text{U}_3\text{O}_8 \) is formed.

Average specific heat for uranium (UO₂) for 10° to 98°C was 0.06190.


When soln. of (NH₄)₂UO₄ 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 UO₂.

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 H₂, followed by cooling in H₂, UO₂ is obtained in pure form, colors are attributed to differences in size of aggregates. Cryst. shape is dependent upon prep. method; scales with metallic luster were obtained. Not attacked by dil. HCl and H₂SO₄, even when acids are warm. UO₂ is not attacked by gaseous HCl, even at high temps. It will dissolve in concd. H₂SO₄. When uranyl salts are ignited with volatile acids, U₃O₈ formed is usually accompanied by black U₂O₃.


Reaction product obtained in prep. of UO₂ by igniting uranyl oxalate in dry H₂ is first black and then cinnamon-brown. Pyrophoric and oxidizes rapidly when heated in air. Density = 10.15. Very pure UO₂ in cryst. form obtained by using five parts Na₂UO₄ with 20 parts of anhyd. MgCl₂ in covered crucible. Brilliant black cubes are obtained, easily isolated because of great dens. and stability in presence of dil. acid. When mixed U₄O₁₄·6 H₂O, 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 U₃O₈ = 7.31. Prick-red product obtained by dehydration of UO₃·H₂O at 300°C identified as U₂O₇ which goes to U₃O₈ at red heat. Question is raised re actual existence of U₂O₅ proposed by other investig. Paper contains discussion of solubility of U₃O₈ in acids.

Method described by Wohler for preparing $\text{U}_3\text{O}_8$ using $\text{NH}_4\text{Cl}$ and $\text{NH}_4\text{UO}_4$ yields an oxynitride of $\text{U}$ rather than $\text{UO}_2$. Expts. on the method fail to confirm results.


$\text{UO}_3$ reacts with gaseous mix. of $\text{CO}_2$ and $\text{CS}_2$ at red heat and will form $\text{UO}_2$. Very pure $\text{UO}_2$, in cryst. form, obtained by heating five parts of $\text{Na}_2\text{UO}_4$ with 20 parts of anhyd. $\text{MgCl}_2$ in a covered crucible. Brilliant black cubes obtained easily isolated because of great density and stability in presence of dil. acid. $\text{UO}_2$ obtained by ignition of $\text{U}_3\text{O}_8$ or $\text{Na}_2\text{UO}_4$ with $\text{S}$ or $\text{NH}_4\text{Cl}$, followed by water leaching.


$\text{UO}_2$ obtained by igniting $\text{U}_3\text{O}_8$ which has been moistened with a few drops of HF. Particularly simple method of preparing black crystalline $\text{UO}_2$.


$\text{UO}_2$ prep. by reduction of oxalate is reported to dissolve in an ammoniacal soln. of $\text{AgNO}_3$, with the pptn. of metallic Ag.


Brown $\text{UO}_2$ obtained by reducing $\text{UO}_3$ with $\text{H}_2$ at red heat. Not attacked by $\text{N}_2\text{O}$ at 150$^\circ$C, whereas black $\text{UO}_2$ prep. at a lower reduction temperature is slowly oxidized by $\text{N}_2\text{O}$ to $\text{U}_2\text{O}_5$.


$\text{NO}$ will react with brown $\text{UO}_2$ below red heat, with evolution of light and formation of black $\text{U}_2\text{O}_5$. Brown $\text{UO}_2$ obtained by reducing $\text{UO}_3$ with $\text{H}_2$ at red heat. Not attacked by $\text{N}_2\text{O}$ at 150$^\circ$C, whereas black $\text{UO}_2$ prepared at a lower reduction temp. is slowly oxidized by $\text{N}_2\text{O}$ to $\text{U}_2\text{O}_5$.

When $\text{UO}_2\text{Br}_2$ is calcined in air, Br is split off and brick red $\text{UO}_2$ remains. In contrast to product obtained from $\text{UO}_2\text{Cl}_2$, $\text{UO}_2$ obtained is oxidized to green $\text{U}_3\text{O}_8$. When material is heated in stream of hydrogen, brick-red $\text{UO}_2$ goes to black modification. Use of calcining method for U detn. is described.


Thermal decomposition of $\text{UO}_2$ begins in vacuum at about 1600°C. When mixture of $\text{UO}_2$ and C is heated electrically in vacuum, reduction begins at about 1490°C where increase in pressure due to evolution of CO occurs.


$\text{UO}_2$ obtained by reduction with $\text{H}_2$ at low red heat of orange-red $\text{UO}_3\cdot\text{H}_2\text{O}$. Dark brown $\text{UO}_2$ obtained was converted slowly by $\text{H}_2\text{O}_2$ into the hydrate $\text{UO}_2\cdot\text{H}_2\text{O}$, which oxidized to $\text{UO}_3\cdot\text{H}_2\text{O}$ and small amount of green dihydrate. If $\text{UO}_2$ was heated with $\text{H}_2\text{O}_2$ almost to the b.p., oxidation was completed more rapidly. With very dil. $\text{HNO}_3$, $\text{UO}_2$ was hydrolyzed; if heated gently it dissolved without oxidizing. By heating to 105° to 110°C, $\text{UO}_2\text{SO}_4\cdot3\text{H}_2\text{O}$ lost 2$\text{H}_2\text{O}$; heated higher, some $\text{H}_2\text{SO}_4$. If dry salt is heated to low redness it decomps. into $\text{UO}_3$ and $\text{SO}_3$; at red heat it becomes $\text{UO}_2$, $\text{SO}_3$, and $\text{O}_2$; $\text{UO}_2$ oxidized to green $\text{U}_3\text{O}_8$. Strongly heated with $\text{H}_2$, black $\text{UO}_2$ was set free from $\text{UO}_2\text{SO}_4$. If heated, uranous was converted at low redness to uranic salt; further $\text{UO}_2$ was formed, which was converted to $\text{U}_3\text{O}_8$, then $\text{U}_4\text{O}_{10}$. U acetate, by dry distillation, gave $\text{CO}_2$, acetone, $\text{H}_2\text{O}$, and $\text{H}_2\text{CO}_3$ besides black (including brown) $\text{UO}_2$, which, heated in air, oxidized. If acetate is heated in air, true black $\text{UO}_2$ was formed.


Actions of $\text{UO}_2$ and $\text{UO}_3$ are discussed along with other metal oxides. Trials of $\text{UO}_3$ on ethyl, methyl, and benzyl alcohol are described. $\text{UO}_2$ 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 $\text{UO}_2$ determined by reduced $\text{UO}_2\text{Cl}_2$ with $\text{H}_2$ according to the equation: $\text{UO}_2\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl} + \text{UO}_2$. Five determinations gave mean value of 270.07.


Pure $\text{UO}_3\cdot\text{H}_2\text{O}$ was reduced with $\text{H}_2$ at bright-red heat. Using 238.5 as at. wt. of U and 304.5 as mol. wt. of $\text{UO}_3\cdot\text{H}_2\text{O}$, means of 5 detns. gave 270.66 as mol. wt. of $\text{UO}_2$, the theoretical value being 270.5.


Soln. by wt. in $\text{HCl}$, HBr, $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, $\text{HOAc}$, and aqua regia are reported to be $\text{UO}_2$; 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. $\text{UO}_2$ was obtained by calcining $\text{UO}_2\cdot\text{C}_2\text{O}_4$, which had been purified by several crystns., in a closed crucible.

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

By electrolysis of soln. of $\text{UO}_2\text{Cl}_2$ a black ppt. forms, sol. in $\text{H}_2\text{O}$ 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 $\text{UO}_2$. Reduction of $\text{UO}_2\text{Cl}_2$ by Zn or Cu in dil. $\text{HCl}$ soln. gives same colloidal soln; reduction of sulfate fails, probably because of soly. of colloid in $\text{H}_2\text{SO}_4$.

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

$\text{UO}_2$ was obtained by heating pure green oxide in a current of $\text{H}_2$, also, by heating $\text{UO}_2\cdot\text{C}_2\text{O}_4$ in a current of $\text{H}_2$ at a lower temp. Obtained by latter method, found to be more sol. in $\text{HCl}$ than by former. Both forms are slightly soluble in $\text{HCl}$ if allowed to react a long time (2 to 28 weeks). Results reported by Raynaud are low because time of solution was too short.


$\text{UO}_2\cdot\text{C}_2\text{O}_4$, recrystd. several times, contains 3 moles $\text{H}_2\text{O}$. Sol. in $\text{H}_2\text{O}$ but slightly sol. in $\text{EtOH}$ or $\text{MeOH}$. $\text{H}_2\text{O}$ escapes when salt
423—Continued

is heated to 100° for 4 hours. Upon calcination, pure UO₂ is left in form of black powder, not readily sol. in hydroacids or in H₂SO₄, but readily sol. in HNO₃ 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 UO₂ is formed and, consequently, UO₃.


Graph showing sol. of UO₂. Density of UO₂ is 8.2.


Finely divided UO₂ or UO₃ when dispersed in strong blast of air, will acquire positive charge of static electricity. Many other materials were also investigated.


UO₂ may be prepared by fusing Na₂U₂O₇ with NaCl and charcoal. Permits recovery of vanadic acid which may be contd. in Na₂HVO₄ as an impurity.


Pgs. 251-2 contain information on attempts made to confirm early work of Pegnault (1836) on oxidation of UO₂ by H₂O vapor. Expts. reported by early experimenter showing U₃O₈ could not be duplicated.


When UO₂ is heated in O₂, it will oxidize to U₃O₈ within a very narrow temp., beginning at 185°, without appearance of any intermediate oxide phase. Reduction of damp or dry UO₃ or U₃O₈ in stream of H₂ will yield very pure UO₂. Reduction is carried out at 900° to 1200°C. UO₃ heated in vacuum at 500° begins to go over to U₂O₅; decomposition is not reversible. Reduction of U₃O₈ in H₂ atm. at 625° to 650°C was found to be successful. It is quantitative if H₂O produced is continually removed by P₂O₅. No other
reaction takes place as high as 1000°C. If U₃O₈ is heated in vacuum for about 3 hours at 1000°C, it will lose oxygen to composition of about UO₂.42. To prepare nitrate-free UO₃, decomp. must be carried out at about 500°C.


Powdered gray product is obtained, which will not lose weight at 1000°C, when U₃O₈ is heated to 800°C. Discussion of reduction of damp or dry UO₃ or U₃O₈ in stream of H₂ which yields very pure UO₂. Reduction is carried out at 900°C to 1200°C. UO₂ product is chestnut-brown and reduction was found to begin at about 500°C. Examination of method of heating U₃O₈ with a few drops of HF in order to prepare UO₂: however, method does not prevent reoxidation to U₃O₈ in O₂. Regardless of prepn. method, true UO₂ is brown. UO₃ shows no noticeable change when heated in air to 600°C; decomposition is evident at 700°C, and is rapid and complete at 800°C. U₂O₈ prepd. below red heat will never be completely pure, always containing some UO₃. UO₃ in moist air, at ordinary temps., was found to go to UO₃.2H₂O. U₃O₈, prepd. by heating uranyl oxalate in covered crucible at 350°C, is grayish-black. If product is heated for 12 hours in air at 350°C, it turns orange-brown and shows almost exactly increase in wt. which would be required to convert it to UO₃.


Minerals pitchblende, broggerite, cleveite, and thorianite, and pure oxides UO₂, UO₃, U₃O₈, ThO₂ and CeO₂ 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. UO₂, ThO₂ and CeO₂ 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 U₃O₈ is essentially different from that of UO₂, and crystals do not belong to
430—Continued

isometric system. UO₃ 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 UO₂, ThO₂, some CeO₂, and eventually to dioxide of U-Pb. Therefore, broggerite and other varieties of uraninite do not belong to spinel group. Lattice dimensions (km units) were thorianite = 5.57, broggerite = 5.47, cleveite = 5.47, and UO₂ = 5.47. Cleveite, which is rich in UO₃, is transformed to U₃O₈ by heating to 800°C. Broggerite, after heating, has structure of UO₂. 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 10⁻⁸ cm, therefore, smaller than those of pure UO₂, perhaps in consequence of isomorphic replacement of U by an atom of smaller vol. Probably taking up of an excess of O₂ in crystallization of UO₂ 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.


UO₂ was found to be stable to H₂ even at high pressure (25 atm) and high temps. (m.p. of W).


Unit cell of wolfram (UO₂) is 3.15 A, a is 5.48 km, used CuKα radiation.


UO₂ (brown in H₂ and blue in N₂) was prepd. from U₃O₈. Hardness of about 5 and melts from 2500°C to 2600°C. Electrical resistance is very high.

434—Continued

Discussion of crystal structure of UO₂. Empirical calculation of radius of U⁴⁺ ion in crystal lattice yields 0.97Å. For UO₂ of fluorite-type structure, the lattice ratio is reported as 0.69.


Interatomic distance in UO₂ (2.37 kX) and assumed radius for U⁴⁺ (1.22 kX) are reported. Structure type (I) and ratio of atomic radii (0.94) are also reported for UO₂.


Curve of surface tension of 1% UO₂ soln. as function of temp. shows max. at 30° to 40°C. Stability of soln. is examined over range 10° to 70°C.


W lamp filament and Fe wire in H₂ gave positive temp. coeff. To meet demand for convenient neg. temp. coeff. resistor, UO₂ resistors were developed. Ohmic resistance is practically const. even after many thousand hrs. of service. UO₂ unit is mounted in lamp bulb filled with N₂ 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, UO₂ 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 UO₂ 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.


Electrical resistance with neg. temp. coeff. and for use particularly with Fe-H resistors is prepared from UO₂.


Lattice is fluorite type with space group O₅-Fm3m and four molecules per unit cell, a = 5.48 Å (converted from kX).
440. THE MEASUREMENT OF THE DIELECTRIC CONSTANT IN THE CENTI-
Phys. Soc. 51, 679 (1939)] dielectric constant in the cm band was
determined for UO₂ 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.

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
density of 2000 to 3000 cps. Non-reversible characteristics and low
limiting freq. were obtained with sintered UO₂ (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. (Splin-
ters laid on top of glazed electrical porcelain and heated until
splinters were imbedded in molten glaze.) Effect of neg. resist-
ance 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. P. Giles, and N. L. Lofgren. MDDC-193, July 24, 1945, de-
classified Aug. 17, 1946. Methods for prepn. of US₂S₃ and US₂ are reported. US₂ and
intermediates of US₃ are prepd. by H₂S treatment of UO₂ or U₃O₈
in C system at 1200° to 1300°C. In this method US₂ is an inter-
mediate and C of system enters reaction in its conversion to pure
sulfides.

443. ELECTRICAL RESISTANCE OF THE CONTACT BETWEEN A SEMI-
Contact resistance and potential of semiconductor and metal
were investigated with currents in both directions. For semi-
conductor UO₂ it was found that, close to metal, there arises
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.


High-temperature heat contents of U, UO₂, and UO₃ 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:

for UO₂, \( H_T - H_{298.16} = 19.20T + 0.81 \times 10^{-3}T^2 + 3.957 \times 10^5T^{-1} - 7124(298-1500°K) \ 0.1\% \)

for UO₃, \( H_T - H_{298.16} = 22.09T + 1.27 \times 10^{-3}T^2 + 2.973 \times 10^5T^{-1} - 7696(298-900°K) \ 0.1\% \)

These yielded following equations for heat content:

\( UO₂, C_p = 19.20 + 1.62 \times 10^{-3}T - 3.957 \times 10^5T^{-1} \)

\( UO₃, C_p = 22.09 + 2.54 \times 10^{-3}T - 2.973 \times 10^5T^{-1} \)

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


Ignition assay of brown oxide for free UO₂ is subject to error due to tendency of powdered material to adsorb \( H₂O \). 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, UO₂, AND UO₃.

Consists of tables giving heat contents of U, UO₂ and UO₃ above
298.16°K (400° to 1500°K) as obtained from smooth curves and from
experimental results.

447. OXIDATION OF URANIUM DIOXIDE (UO₂), F. Gronvold and H.

UO₂ (a = 5.468A, converted from kX) was heated in oxygen from
100° to 265°C, and products examined by x-ray powder method. At
156°UO₂ takes up oxygen to UO₂.₃₄. Change to lower symmetry is
indicated (a = 5.40 kX). Change from UO₂ to UO₂.₃₄ is accompanied
by an increase in density from 10.80 g/cc. In the range 200° to
250°C, oxygen exceeds UO₂.₃₄ 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 UO₂.₃₄ = 11.46;
U₀.₈₂O₂.₁₂ = 10.04; U₀.₈₂O₂ = 9.44. U atoms form face-centered
lattice (0,0,0; ½,½,0; ½,0,½; ½,0,½). Observed and calculated
intensities are in good accord. Phase near composition U₂O₅ was
found, stable below 260° to 270°, as a tetragonal deformed UO₂
with composition not to exceed U₀.₈₈O₂.₁₂. U₃O₈ has homogeneity
between U₂O₅ and UO₂.₅₆.

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.

To extend scope of information of physicochemical properties of
U dusts, surface area measurements were made on several representa-
tive U compounds. Experimental method most suitable to purpose
was found to be low-temperature gas adsorption. Using modified ap-
paratus developed by Wooten and Brown, C₂H₆ (at -183°C) was chosen
as adsorbate in order to evaluate very small surface areas encontra-
ted. U compounds investigated were UO₂, UO₃, UO₄. With excepti-
on of UO₄, all compounds exhibited fairly low specific surfaces
of order of from 0.4 to 0.7 m²/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 suspen-
sions of fine and coarse UO₂ dust. Fine material showed tenfold
larger area of 4.23 m²/g as compared with 0.47 m²/g for coarse
suspension. Corresponding calculated specific surfaces, however,
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).


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\(_2\)C\(_3\)) from oxides UO\(_2\) or U\(_2\)O\(_3\) 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.


UO\(_2\) prepared from UO\(_4\) by thermal reduction with H\(_2\) (heated to 350°C and exothermic reaction raised temperature to 900°C 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.


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 \(\beta\)-UO\(_2\). Oxides in composition range UO\(_2.2\) to UO\(_2.3\), prepared below 230°C, have tetragonal structure with axial ratio...
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.


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%.


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$_2$O, ppt. the $UO_2(NO_3)_2$ as $UO_4$ with $H_2C_2$, converting $UO_4$ to $UO_2$ 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.


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.

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 anhydrous $UO_3$ 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$_2$O$_8$ were compared. Former showed region of stability corresponding to formula $UO_{2.9}$. 

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.

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$_3$N$_2$, TaN, and ThN is presented. Evidence is given indicating that the hexagonal structure reported by others for TaN is actually that for Ta$_2$N. Lattice for Th$_2$N$_3$ is proposed. Melting points of ThN, UN, and UC are determined to be 2630° ±50°C, 2150° ±100°C, and 2590° ±50°C, respectively.

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
459—Continued
alumina. Shapes of curves for UO₂ 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 phenomenon and pH-solubility curve for silver oxide. Satisfactory UO₂ crucibles can be made by slip casting at pH 2.1.


Precise measurements of heats of combustion of Th, U, and U dioxide made and heats of formation of ThO₂, UO₂, and U₃O₈ calculated. Final values for the various materials are: thorium, heat of combustion in 25 atm. oxygen = 5276 ± 7 joules/g.; heat of formation of ThO₂, ΔH₂₅⁰C = −1227.4 ± 1.5 kJ/mole; uranium dioxide, heat of combustion in 25 atm. oxygen = 380.23 ± 0.46 joules/g.; heat of reaction 3UO₂ + O₂ = U₃O₈, ΔH₂₅⁰C = −318.01 ± 0.37 kJ/mole; uranium, heat of combustion to U₃O₈ in 25 atm. oxygen = 4984.7 ± 0.7 joules/g.; heat of formation of U₃O₈, ΔH₂₅⁰C = −3570.9 ± 6.9 kJ/mole. It was necessary to cut U into small pieces and mix with UO₂ in order to oxidize it completely to U₃O₈. Heat of formation of UO₂ calculated is ΔH₂₅⁰C = −1084.3 ± 2.5 kJ/mole.


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 UO₂, UO₃, U₃O₈, and hard lustrous uraninite shown diagrammatically. Differential thermal curves are illustrated.
representing uraninite specimens, thorianite, and oxides \( \text{UO}_2 \), \( \text{UO}_3 \), and \( \text{U}_3\text{O}_8 \). 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 \( \text{UO}_2 \) 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 \( \text{UO}_2 \) in temperature range 20\(^\circ\)C to 250\(^\circ\)C was \( 9 \times 10^{-3} \) cgs units.


Existence of tetragonal \( \text{U}_3\text{O}_7 \) in homogeneous phase between \( \text{UO}_2 \) and \( \text{U}_3\text{O}_8 \) is shown by oxidation-reduction and x-ray diffraction experiments. No intermediates, such as \( \text{U}_2\text{O}_5 \), were found between \( \text{U}_3\text{O}_7 \) and \( \text{U}_3\text{O}_8 \). Composition \( \text{U}_3\text{O}_7 \) is difficult to reconcile with concept of definite compound.


Three strongest lines for NBS pattern of \( \text{UO}_2 \) are 111, 220, 200, \( a = 5.4682 \)\( \text{\AA} \), 26\(^\circ\)C. Density calculated from NBS lattice data is 10.968. (To be published as NBS Circular.)


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.


Measurements of transmission of monokinetic neutrons by microcrystalline \( \text{UO}_2 \) and \( \text{CeO}_2 \) 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.


Six specimens of pitchblende analyzed for \( ^{238}\)U and \( ^{238}\)U content and x-ray powder photographs obtained before and after heat treatments. Cell edges of pitchblende range continuously from 5.470 to 5.395 Å. Decrease is due to oxygen entering interstitial positions in UO\(_2\) structure with consequent change of \( ^{238}\)U to smaller \( ^{238}\)U 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 \( ^{238}\)U. 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 UO\(_{3.8}\) 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 \( ^{238}\)U 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 = 5.405Å. 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 UO\(_{3.8}\) powder patterns show double hexagonal cell instead of orthorhombic cell generally associated with UO\(_{3.8}\). Amorphous UO\(_{3}\), reported by Zachariasen, was
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 pitchblends 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. 648.


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 cleanliness).

3.1 Additional references not abstracted


3.1—Continued


"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).


4. **U₂O₅ (500-505)**


UO₃·2H₂O prep'd. by heating finely pow'd. mixt. of U₃O₈ with excess KCIO₃ in Pt crucible and repeatedly leaching melt with water. When UO₃·2H₂O 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. Prep'n. and properties of material which is U₂O₅ is discussed. Attempts to prep. UO₄ by strong oxidation of acid, neutral or alk. soln. of uranics, and uranates are reported, all attempts were unsuccessful.


Question is raised concerning actual existence of compound reported as U₂O₅. Description is included of physical appearance of U₂O₅. 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).

UO₂ was not noticeably affected by light. NO will react with brown UO₂ below red heat with evolution of light and formation of black U₂O₅.


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 U₂O₅ and green oxide U₃O₈ are prep'd. 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.

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 becomes 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.


Complete structure determinations reported for U$_2$O$_5$, and U$_3$O$_8$. Structures of some compounds considered from viewpoint of theory of metals. New method of determining 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

5. $\text{U}_3\text{O}_8$ (600–645)


$\text{U}_3\text{O}_8$ can be reduced to $\text{UO}_2$ by $\text{K}$ at about 150°C. Dull glow is produced during reductions.


$\text{U}_3\text{O}_8$ 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.


$\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ can be converted to $\text{U}_3\text{O}_8$ by ignition with $\text{NH}_4\text{Cl}$.


$\text{U}_3\text{O}_8$ obtained when $\text{UCl}_4$ is ignited in presence of water vapor.


Pure uranyl acetate may be reduced to $\text{UO}_2$ in stream of $\text{H}_2$ and, when product is treated with $\text{HNC}_3$, can be ignited to $\text{U}_3\text{O}_8$. Mean specific heat of $\text{U}_3\text{O}_8$ between 00° and 100°C is 0.7979.


Atomic weight of $\text{U}$ is determined. Sodium uranyl acetate is prepd. by treating pure uranyl nitrate with $\text{Na}_2\text{CO}_3$ and excess boiling $\text{HOAc}$. Microcryst. product dried at 120° to 150°C. Discussion of conversion of $\text{U}_3\text{O}_8$ of ppt. obtained by treating $\text{U}$-contg. soln. with $\text{NH}_3$. If conversion is done in current of $\text{O}_2$, oxide does not have uniform composition; therefore, should first be reduced to $\text{UO}_2$ in current of $\text{H}_2$ and dtm. make on basis of that cpd. $\text{U}_2\text{O}_5$ reported by some investigators is mostly $\text{U}_3\text{O}_8$ with certain amount of $\text{UO}_2$. Pure $\text{U}_3\text{O}_8$ obtained by igniting purest possible uranyl salts to $\text{U}_3\text{O}_8$, reducing raw product with $\text{H}_2$ to $\text{UO}_2$, and reoxidizing with pure $\text{O}_2$ to $\text{U}_3\text{O}_8$. Product should cool in stream of $\text{O}_2$. Color of resulting material, which may be olive green to black, is influenced strongly by method of prep. and heat of reduction. When
U₃O₈ is ignited and cooled quickly in air, will lose small quantities of O₂. Losses are greatly increased if cooling takes place in gas such as N₂ or CO₂ which are inert. When U₃O₈ is ignited in such atmospheres brown UO₂ is obtained. Green liquid is obtained with HCl when U₃O₈ is dissolved in closed system (temp. approx. 200°C). Completely converted to uranyl and U₄ sulfate when heated with concd. H₂SO₄ for a long time.

   When U₃O₈ is heated with KClO₃ reaction involves loss of O₂ with evolution of a great deal of Cl₂ and formation of K₂UO₄. Reaction was found to begin at approximately 390°C.

   When U₃O₈ is heated with KClO₃ reaction involves loss of O₂ with evolution of a great deal of Cl₂ and formation of K₂UO₄. Reaction was found to begin at approximately 390°C.

   When U₃O₈ is heated with KClO₃ reaction involves loss of O₂ with evolution of a great deal of Cl₂ and formation of K₂UO₄. Reaction was found to begin at approximately 390°C.

   Crystalline mixture of Th-U oxide can be prepared by mixing U₃O₈ and ThO₂ with borax glass in Pt crucible and fusing. When only U₃O₈ is fused oxyhedral crystals consisting of UO₂ accompanied by some UO₃ are obtained. UO₃ present will decrease as fusion continues. Crystals of UO₂ are found to be isomorphous with ThO₂ as determined by preparation of synthetic mixtures.

   Discussion on reduction of U₃O₈ to U metal using sugar-derived C. Impurities found were carbon (13.5 to 2.06 %) and N.

When U₃O₈ is mixed with large excess of NH₄Cl, 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.


Uranium metal is more volatile than iron metal. Preparation of U₃O₈ by ignition of uranyl nitrate, which is easy to obtain pure, is discussed. Ignition is carried out in porcelain crucible.


When UO₂ is exposed to air, slow oxidation takes place in which U₂O₃ is formed. Reduction, at 900° to 1200°C, of damp or dry UO₃ or U₃O₈ in a stream of H₂ will yield very pure UO₂. UO₂ can also be obtained by heating U₃O₈ in vacuum at 2000°C. Forms as rhombic platelets with flattened corners.


Attempts to reduce U₃O₈ with C at current density of 25 amps. did not give complete reduction; 100 amps. at 50 to 60 v. were required.


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 U₃O₈, 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 H₃BO₃ 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 U₃O₈.

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

Prepn. of U, reduction of its oxides with Al is considered. "pure" uranyl salts available in commerce for prepn. of $\text{U}_3\text{O}_8$ always contain alk. in form of double salts. Thus, pure uranyl acetate of Merck and Kahlbaum corresponds to $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2\cdot\text{Na}(\text{C}_2\text{H}_3\text{O}_2)\cdot2\text{H}_2\text{O}$ and give Na pyrouranate, $\text{Na}_2\text{U}_2\text{O}_7$ in ignition. To remove alk. proceed: (1) ignite mass containing alk. pyrouranate in stream of $\text{H}_2$, extract reduction product with $\text{H}_2\text{O}$; or (2) dissolve ignition product containing pyrouranate in acid ($\text{HNO}_3$) and transform into pure NH$_4$-uranate by repeated pptns. with NH$_3$. Latter, on ignition, gives pure $\text{U}_3\text{O}_8$ 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.


Radioactive substances accompanying U in minerals are almost completely removed by ordinary process of prepn. of so-called chemically pure $\text{UO}_2(\text{NO}_3)_2$. Minute traces of Na may be removed by means of BaSO$_4$. Pure $\text{U}_3\text{O}_8$, of perfectly definite composition, is readily obtained by heating nitrate or any lower or higher oxide of U in air at 700°C.


Continuation of work, making use mainly of $\text{Na}_2\text{O}_2$ to carry out reactions. Inability to prepare pure V left results subject to some uncertainty. Among results are $3\text{U} + 4\text{O}_2 \rightarrow \text{U}_3\text{O}_8 + 845,200$ cal.; $\text{U} + 30 - \text{UO}_2 + 303,900$ cal.; $\text{UO}_3 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{UO}_4 + 96,000$ cal.; and $\text{U}_3\text{O}_8 + \frac{3}{2}\text{O}_2 \rightarrow 3\text{UO}_3 + 16,200$ cal.

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 U3O8 and other salts. From data conclusion is drawn that Kopp's law does not hold at low temp., where Dulong and Petit 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.


Description of reduction of U3O8 by Na and Mg in presence of CaCl2 is given. Metal of 99.4 to 99.6% U was obtained.


Several methods for reduction of U3O8 were tried. Best results were obtained by electrothermal-thermite process. Granular resistor used to heat tube of pure MgO which contd. mixt. of 80% U3O8 and 20% Mg powder pressed into form of rods. Ends of rods were placed in contact with C electrodes and current of H2 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. H2 was displaced by CO2 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% U3O8, 15% CaCl2, 15% Mg, and 20% Na in steel cylinder to bright-red heat.


U3O8 will not be reduced by H2 any further than UO2 when heated as high as 2500°C at pressures up to 150 atmospheres.


Discusses prepn. of U3O8 and mentions that classical method which used uranyl nitrate extraction with Et2O contains disadvantage of danger of explosion during purification process. Proposes
that alk.-free U₃O₈ cannot be obtained by this method. Alk.-free products obtained by recryst. nitrate several times in H₂O as follows: slight excess of carbonate-free NH₃ is added and soln. is satd. with H₂S. Then, heated to boiling without interruption of H₂S and ppt. is washed well with water contg. (NH₄)₂S, sucked dry in filter and dissolved in small quantity of concd. HCl. Dark-green UCl₄ is formed. H₂S is driven off by boiling the soln., and further treatment with NH₃ and H₂S is made. UCl₄ soln. is again pptd. with NH₃ and ppt. again dissolved in strong HNO₃. Uranyl nitrate formed is recrystd. from pure H₂O until no free acid remains, and then ignited in normal manner to U₃O₈.


Pitchblende was mineral used in investigation. Method of prepn. pure U₃O₈ for comparison was given.


U₃O₈ 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.


UO₃ was prep'd. from UO₄·xH₂O as orange amorph. material. U₃O₈ prep'd. below 800°C is moss-green; above that temp. is black. UO₂ is brown or dark brown-violet. System UO₃-U₃O₈ is fully discussed. Direct inversion of U₃O₈ into UO₃ is probable in minerals, it is proved for prepns. Observed pressures are not equil. pressures, but are near to them. System UO₃-U₃O₈ is reversible. Discussion of mol. vol. and relations between color and cryst. form is included.


General color effect produced by uranium with the following compounds: CeO₂—dirty green colors, fusion usually incomplete;
628—Continued

CaO—greens and blue greens; CuO—dark green, Fe₂O₃—reddish brown to very dark brown; Mn(OH)₂—dark brown to almost black; TiO₂—brown, fusion usually incomplete; NiCO₃—green spots, does not seem to disperse with main portion of glaze; SnO₂—infusible in these mixtures; ZnO—small amount acts as flux and lightens color; CaF₂—does not affect color, large amounts act as refractory; CaCO₃, BaCO₃, MgCO₃—do not affect color, large amounts act as refractory; Na₂CO₃, K₂CO₃, Li₂CO₃—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)₃ and CdCO₃—intensify or may even darken orange color; and MoO₃ and K₃VO₄—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 (UO₂) 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 (U₃O₈) 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.
Mikiya Akatuska, Ceram. Abs. 2, 142 (1923); Report of the Pottery Laboratory (Kioto) 1, 57 (1922).

Discuss theory of ordered mixed phases in oxides as exemplified by $\text{U}_3\text{O}_8$.

Values for entropy at 298.14K are given for U and $\text{U}_3\text{O}_8$ and as many other materials as necessary data was found. Methods of calcn. are discussed and a bibliography of 400 references is included.

Effect of calcining temperature upon gas-absorbing power of mixtures $\text{Co} + \text{Cu} + \text{U}_3\text{O}_8$ in range 200° to 300°C, and $\text{Co} + \text{U}_3\text{O}_8$ and $\text{Co} + \text{ThO}_2$ in the range 250° to 450°C contg. various amounts of
632—Continued

diatomaceous earth was studied. Gas used was mixture CO + H₂ 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.
2, 1946.

X-ray patterns are given in tabular form for UO₂, U₃O₈. Dis-

cussion 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

To obtain data that would be useful in predicting changes that
might be expected to occur in oxidation state and degree of hydra-
tion of powdered U oxides maintained for long periods of time at
temperatures between 30⁰ and 300⁰C in presence of excess water,
hydrogen, oxygen, and possibly H₂O₂. Reaction of hydrogen and
oxygen with water slurries of UO₃ were studied at 100⁰ to 300⁰C.
Rates of reactions appear to fit an equation of form

\[-d(1 - x)/dt = kp^n (1 - x)^\theta,\]

where x is fraction of U⁶⁺ or U⁴⁺ 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, dif-
ficulty encountered by gas molecules in penetrating solid parti-
cles, or some equivalent phenomenon. Oxidation reaction appears
to be first order with respect to O₂ (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, ac-
tivation energy is 10,000 cal (15%). U₃O₈ 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 250⁰C,
under 16.4 atms. of hydrogen reduction reaction is only 5 to 6%
complete in 2 hours at 250⁰C. Difference in rate is due largely
to difference in theta for two reactions; that is, rate of reduc-
tion reaction decreases more rapidly with decrease in "available
oxide surface" than does rate of oxidation reaction. UO₃.H₂O was
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.


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 $U_3O_8$.


$U_3O_8$ or amorphous $UO_3$ heated in oxygen under pressure of 30 to 150 atm. at temp. of 500° to 750°C are converted to crystalline $UO_3$, three varieties are formed. Least stable is hexagonal $UO_3$. 68
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 $UO_2.95$, 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 $U_3O_7$ with HNO$_3$ gave x-ray patterns different from those of any of 3 phases prepared by ignition of $U_3O_7$ in O$_2$ under high pressure. One sample when treated at 600°C with O$_2$ at atmospheric pressure “disproportionated” into mixture of $U_3O_4$ and “Mallinckrodt” $UO_3$.


Single $U_3O_8$ crystals could not be prepared; however, one preparation gave X-ray photographs in which reflections with indices (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 $PeO_3$ structure, but with deformed $(UO_6)^{14-}$ octahedrons with anion vacancies.


$U_3O_8$ 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$_2$O containing 5 ml water, and removing uranyl nitrate from Et$_2$O 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—
(1949).

Study of gravimetric methods for determination of U⁴⁺ and U⁶⁺;
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:

<table>
<thead>
<tr>
<th>Pptg. reagent</th>
<th>Form weighed</th>
<th>Temp. limits, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium hydroxide</td>
<td>UO₃</td>
<td>480 to 610</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>UO₂</td>
<td>745 to 946</td>
</tr>
<tr>
<td>Ammonia (gas)</td>
<td>U₃O₈</td>
<td>675 to 946</td>
</tr>
<tr>
<td>Pyridine</td>
<td>U₃O₈</td>
<td>745 to 946</td>
</tr>
<tr>
<td>Ammonium benzoate</td>
<td>U₃O₈</td>
<td>691 to 946</td>
</tr>
<tr>
<td>Hexamethylenetetramine</td>
<td>U₃O₈</td>
<td>745 to 946</td>
</tr>
<tr>
<td>Tannin</td>
<td>U₃O₈</td>
<td>570 to 875</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>U₂O₃</td>
<td>811 to 946</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>U₂O₃</td>
<td>811 to 946</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>U₃O₈</td>
<td>850 to 946</td>
</tr>
<tr>
<td>Disodium phosphate</td>
<td>U₂P₂O₇½</td>
<td>673 to 946</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>U(C₂O₄)₂</td>
<td>100 to 180</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>U₂O₆</td>
<td>700 to 946</td>
</tr>
<tr>
<td>Cupferron</td>
<td>U₃O₈</td>
<td>800 to 946</td>
</tr>
<tr>
<td>Beta-isatoxine</td>
<td>U₂O₆</td>
<td>408 to 946</td>
</tr>
<tr>
<td>8-hydroxyquinoline</td>
<td>H(UO₂(C₉H₆ON)₂)</td>
<td>&lt; 157</td>
</tr>
<tr>
<td>8-hydroxyquinoline</td>
<td>U₂O₆(C₉H₆O₇)₂</td>
<td>252 to 346</td>
</tr>
<tr>
<td>Quinaldinic acid</td>
<td>U₃O₈</td>
<td>610 to 946</td>
</tr>
</tbody>
</table>

640. ON THE REVERSIBILITY OF THE REACTION 3UO₃ ⇌ U₃O₈ + O₂,

Authors previous work [Compt. rend. 227, 1365 (1948)] formation
of solid solution UO₂·₉₀, stable at 520° to 610°C, was recognized
as intermediate stage in decomposition of UO₃. Present paper condi-
tions of reverse reaction are described, viz., of reoxidation of
U₃O₈ and of solid solution. X-ray spectra of U₃O₈ revealed exist-
ance 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 UO₂·₉₀ could not be observed in experimental conditions
used for other oxides.

Earlier experiment by one author had shown that uranium boride, UB₄, could be formed by electrolysis of bath of molten borate and alkline earth fluorides in soln. with quantity of U₃O₈

[Andrieux, Ann chim. 10, 423 (1929)]. Attempt was made to prepare new borides of U by varying concentrations of borate and U₃O₈ in bath and by substituting MgFe₂ for alkaline earth fluorides. In first attempts concentration of U₃O₈ was too great in respect to borate, and only UB₄ was formed. When concentration of U₃O₈ was reduced to as much as 1/40 to 2 moles of borate, there resulted a mixture of UB₄ with a new boride UB₁₂. Borides can be separated by use of concentrated HCl or H₂SO₄, since UB₄ is easily attacked by these while UB₁₂ is very resistant to acids.


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 U₃O₈ 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.


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 U₃O₈ and UO₂ resulting from fritting at various temperatures of calcined UO₂(NO₃)₂. Coefficients for these samples were determined at 375°C. Transformations indicated by changes in coefficients of expansion were observed and discussed.

Uranium for Kjeller pile was obtained from uraniferous pegmatite deposit at Einerkilen in Evje in Setesdal, Norway. Process used to obtain pure $\text{U}_3\text{O}_8$ from ore concentrate is discussed. Ore was treated with warm dilute $\text{HNO}_3$, Ra was pptd. with $\text{Na}_2\text{SO}_4$ after addition of $\text{Ba(NO}_3)_2$, and I was pptd. as ammonium uranate, which was transformed to $\text{U}_3\text{O}_8$ 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.


Weissenberg films of $\text{U}_3\text{O}_8$ 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 $\text{U}_3\text{O}_8$) 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 necessitating change of some $\text{U}^{4+}$ to $\text{U}^{6+}$. Space group assigned $\text{C}\overline{6}2\text{m}$. Hexagonal cell contains 1/3($\text{U}_3\text{O}_8$). Suggested that true hexagonal "c" dimension is actually 3 x 4.14 A, measured value being a strong pseudo-period resulting from arrangement of uranium atoms in structure. Two suggestions offered to account for two-cell structure of $\text{U}_3\text{O}_8$: 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 $\text{U}^{4+}$ ions to smaller $\text{U}^{6+}$ ions, may result in a shrinkage of cell as it does in case of $\text{UO}_2$ structure. Suggestions called for two similar oxide structures with greater and less oxygen than resultant $\text{U}_3\text{O}_8$. See also abst. No. 468.

5.1 Additional references not abstracted


5.1—Continued


6. \(\text{UO}_3\) (700-732)

700. ON THE COMPOUNDS OF PHOSPHORIC ACID AND ARSENIC ACID WITH URANUM OXIDE. INVESTIGATION 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 \(\text{UO}_2\text{H}_4\text{(PO}_4\text{)}_2\cdot 3\text{H}_2\text{O}\) is reported. Obtained by heating small amounts of \(\text{H}_3\text{PO}_4\) with \(\text{UO}_3\) to boiling and allowing to stand over \(\text{H}_2\text{SO}_4\). 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 \(\text{H}_3\text{PO}_4\). Alk. soln. does not affect material but alk. fusion will decomp. it. Reduced to \(\text{UO}_2\) when fused with carbonized potassium sodium tartrate.


Yellow U oxide \(\text{(UO}_3\text{)}\) is volatile at approximately 2500 to 3000°C. Probably refers to decomp. product of \(\text{UO}_3\) rather than to \(\text{UO}_3\) itself.

702. ON THE SPECIFIC VOLUMES OF OXIDES, B. BRAUER AND J. I. WATTS. Phil. Mag. 11, 60 (1881).

Specific gravity (5.14) and specific volume (56.03) are reported for \(\text{UO}_3\).


If Zn is used to reduce soln. of \(\text{(UO}_2\text{)}^2^+\), reduction is carried to \(\text{U}^{3+}\) stage rather than stopping at \(\text{U}^{4+}\). Red HCl soln. characteristic of trivalent state can be prepd. by reducing \(\text{UO}_2\text{Cl}_2\) with Zn and HCl. Discussion of absorption spectra of \(\text{U}^{3+}\), \(\text{U}^{4+}\), and \(\text{(UO}_2\text{)}^2^+\) in aq. soln. Titration of U soln. after reduction to \(\text{U}^{3+}\) state with Zn-amalgam using \(\text{K}_2\text{Cr}_2\text{O}_7\) and diphenylamine as an indicator is discussed. Method for prepg. pure \(\text{UO}_3\) from commercial uranyl hydroxide using warm HCl soln. std. with \(\text{H}_2\text{S}\) to ppt. As\(_2\)S\(_3\) and small ants. of other sulfides present is given. Filtrate is treated with \(\text{NH}_3\) and excess \((\text{NH}_4\text{)}_2\text{CO}_3\) after warming with \((\text{NH}_4\text{)}_2\text{S}\). Ppt. formed is filtered off and soln. is acidified with HCl. Dissolved CO\(_2\) is eliminated by boiling and U pptd. as chocolate-brown \(\text{UO}_2\text{S}\) by adding \(\text{NH}_3\) and \((\text{NH}_4\text{)}_2\text{S}\). Ppt. is converted to oxide and raw \(\text{U}_3\text{O}_8\) is dissolved in HNO\(_3\), filtered.
evapd. and crystd., and uranyl nitrate dissolved in Et₂O. Filtrate is then evapd. to dryness and residue ignited strongly. UO₃ will combine with bases forming uranates. UO₃ is slightly acid material in contrast to UO₂ which is strongly basic. Prepn., properties, and crystal characteristics of Li, K, and Na uranates and diuranates are discussed.


When UO₃ is heated for about 8 hours in closed tube at 370° to 380°C. with SiCl₄, Cl₂ and a residue containing unchanged UO₃, UCl₄, UO₂Cl, and SiO₂ are obtained.


Action of NO on UO₃ is compared with action of air (heat to 500°C). First yields black U₂O₅; second, yellow-brown U₃O₈.

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

UO₃ prepd. by decomposition of nitrate at 300°C may be freed of N₂ 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. UO₃ still will contain small traces of NH₃. Prolonged heating of UO₃ and CO₂ is reported to give a pure, mossy-green U₃O₈. Prolonged heating of UO₃ in O₂ will produce detectable amounts of O₃. When UO₃ is heated with KClO₃, K₂UO₄ and free Cl₂ are formed. When UO₄.2H₂O is heated slowly in stream of CO₂ as high as 150°C, it will not lose H₂O and undergoes no visible change. Above 150°, however, will lose H₂O and O₂ and go to orange-yellow UO₃ without forming any ozone.


UO₃ can be reduced smoothly in vacuum with Ca to a product (powder) 98.7 to 99.4% U.


Crystals of UO₂(NO₃)₂.6H₂O 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 UO₃ by Rudge is said to be characterized...
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).

\[ \text{UO}_3, \text{ prepd. in usual way, contains} \ H_2O \text{ and} \ N_2; \text{ to obtain pure} \]

\[ \text{compound it is necessary to heat for some time at} \ 500^\circ C. \text{ in current of} \ O_2. \text{ In contact with} \ H_2O \text{ vapor,} \ UO_3 \text{ is rapidly transformed into} \ UO_2(OH)_2. \]


Monohydrate is quite stable and may be formed by allowing anhydride to remain in moist atm. for short time. Dihydrate is formed by allowing \( \text{UO}_3 \) to remain in moist atm. for several days, it loses 1 mole of water in \( \text{H}_2\text{SO}_4 \) 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 \( \text{UO}_2 \) are discussed.


Formation of a compound of \( \text{BaO} \) with \( \text{UO}_3 \) was indicated. Lists host of other oxides reacted with \( \text{BaO} \).


Discussion on dissociation of \( \text{UO}_3 \) from point of view of valence isobars.


Discusses compn. curve of hydrated \( U \) oxides, particularly \( \text{UO}_3 \) and \( \text{U}_3\text{O}_8 \). Heat of formation for \( \text{UO}_3\cdot\text{H}_2\text{O} \) was obtained from calorimetric measurements of heat of neutralization: \( \text{UO}_3 + \text{H}_2\text{O}(1) \rightarrow \text{UO}_3\cdot\text{H}_2\text{O} \text{(s)} + 4.957 \text{ kcal} \). Heat of formation for \( \text{UO}_3\cdot2\text{H}_2\text{O} \) is calculated to be +7.428 kcal.

714—Continued

UO₃ (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 UO₃. 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.


Thermal decomposition of UO₃ begins at 600°C and is complete at 865°C. Reaction product is first green and then black, forming U₃O₈ as end product. Table shows reactivity of UO₃ with metal oxides when heated at 600°C, 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 UO₃ was heated with BeO, La₂O₃, CeO₂, and MoO₂.

<table>
<thead>
<tr>
<th>Initial materials</th>
<th>Temp. at which reaction begins (°C.)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>Li₂CO₃ + UO₃</td>
<td>380</td>
<td>Light yellow</td>
</tr>
<tr>
<td>Ag₂O + UO₃</td>
<td>150</td>
<td>Green</td>
</tr>
<tr>
<td>CaO + UO₃</td>
<td>160</td>
<td>Light yellow</td>
</tr>
<tr>
<td>BaO + UO₃</td>
<td>240</td>
<td>Light yellow</td>
</tr>
<tr>
<td>SrO + UO₃</td>
<td>125</td>
<td>Light yellow</td>
</tr>
<tr>
<td>MgO + UO₃</td>
<td></td>
<td>Light yellow</td>
</tr>
<tr>
<td>ZnO + UO₃</td>
<td>200</td>
<td>Light yellow</td>
</tr>
<tr>
<td>CdO + UO₃</td>
<td>425</td>
<td>Grayish yellow</td>
</tr>
<tr>
<td>HgO + UO₃</td>
<td>175</td>
<td>Yellowish red</td>
</tr>
<tr>
<td>CuO + UO₃</td>
<td>340</td>
<td>Green</td>
</tr>
<tr>
<td>PbO + UO₃</td>
<td>375</td>
<td>Light yellow</td>
</tr>
<tr>
<td>CeO₂ + UO₃</td>
<td>230</td>
<td>Green</td>
</tr>
<tr>
<td>MnO + UO₃</td>
<td>450</td>
<td>Yellowish green</td>
</tr>
<tr>
<td>NiO + UO₃</td>
<td>340</td>
<td>Yellowish green</td>
</tr>
<tr>
<td>Al₂O₃ + UO₃</td>
<td>450</td>
<td>Light yellow</td>
</tr>
<tr>
<td>Cr₂O₃ + UO₃</td>
<td>230</td>
<td>Green</td>
</tr>
<tr>
<td>Fe₂O₃ + UO₃</td>
<td></td>
<td>Reddish brown</td>
</tr>
<tr>
<td>V₂O₃ + UO₃</td>
<td>290</td>
<td>Light green</td>
</tr>
</tbody>
</table>

Investigation of catalytic effect of UO₃ on oxidation of methane in air. Efficiency of about 10.7%, or of same order as Pt black and Ni, was found. UO₃ was obtained at 325°C. ignition (4 hrs.) of (NH₄)₂UO₄.


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 UC₁₃ and UC₁₄ to U⁶⁺ compound by soln. of FeCl₃ in HCl, or by soln. of IC₁₃, compared with heat of solution of UO₃ in same media. Based on values obtained for heats of formation of UC₁₃ and UC₁₄, heat of formation of UO₃ 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.


Discusses connection between thermochemical properties of UC₁₄ and mol. structure of material, particularly as applied to amines. Total energy change of electronic rearrangement when UC₁₄ is obtained from elements is 930 kcal. For UC₁₃ value calculated as 824 kcal; for UO₃, 1020 kcal; and for UO₂, 695 kcal.


Similarly charged soln. of UO₃ and V₂O₅ react with each other forming colloidal complex UO₃.2V₂O₅. 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—Continued

$\text{V}_2\text{O}_5$ soln. was prep'd. by action of $\text{HCl}$ on $\text{NH}_4$ vanadate and subsequent peptization of ppt. by washing with water. $\text{UO}_3$ soln. was similarly prep'd. from $\text{NH}_4\text{OH}$ and $\text{UO}_3(\text{NO}_3)_2$. 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 $\text{UO}_3.2\text{V}_2\text{O}_5$, addition of more vanadium gives red color, which is unchanged by heating. Absorption spectra and electrometric-titration curves show that $\text{UO}_3.2\text{V}_2\text{O}_5$ is definite complex distinct from original soln. Following formation $\text{UO}_3.2\text{V}_2\text{O}_5$ 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.


$\text{UO}_3$ appears to be a solid-solution of $\text{O}$ in $\text{U}_3\text{O}_8$, and dissociation starting with $\text{UO}_3.04$ proceeds at 580° (15 min.) to $\text{UO}_2.91$ and hence to $\text{UO}_2.84$ (123 hrs.).


$\text{UO}_3$ was found to react with fused $\text{NH}_4\text{NO}_3$ forming $\text{UO}_2(\text{NO}_3)_2$, $\text{NH}_3$, and $\text{H}_2\text{O}$.


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 $\text{UO}_3$ to be 270 kcal/mole.

Values for apparent, or packing density, as well as absolute density have been determined for $^{235}\text{UO}_3$, $^{233}\text{UO}_2$. 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:

<table>
<thead>
<tr>
<th>Material</th>
<th>Analysis (percent)</th>
<th>Absolute density 25°C</th>
<th>Packing density 27.5°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{233}\text{UO}_3$</td>
<td>99.8</td>
<td>7.57</td>
<td>3.95</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td>7.51</td>
<td>(average) 7.54</td>
</tr>
<tr>
<td>$^{233}\text{UO}_2$</td>
<td>99.34</td>
<td>10.26</td>
<td>4.96</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td>10.29</td>
<td>(average) 10.28</td>
</tr>
</tbody>
</table>


Very pure hydrated U oxide was obtained electrolytically from 10% solution of $\text{UO}_2(\text{NO}_3)_2$, by method described by Jolibois [Compt. rend. 215, 319 (1942)]. It loses water, in air, at 380° to 390°C. At higher temps. $^{233}\text{UO}_3$ is transformed into $^{233}\text{U}_3\text{O}_8$. 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; ($^{233}\text{UO}_3$ 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 $\text{UO}_2$.90.

Process for preparation of UO₃ in crystalline form from amorphous U₃O₈. 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 O₂ pressures between 60 and 150 atmospheres at temperature from 700° to 750°C. Description of apparatus for preparation of UO₃ is given.


Experiments investigating decomposition of uranyl oxalate with and without vacuum, decomposition of uranyl oxalate by reduction, and reduction of UO₃ with CO are discussed. X-ray spectra of resulting U oxides compared. Explanation of mechanism decomposition of U oxalate is attempted.


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) UO₂ has zero absorption; (2) UO₃ shows strong absorption which decreases rapidly as temperature is lowered; (3) absorption curve for U₃O₈ goes through min. and then max. as temperature is lowered, which cannot be attributed to electronic origin. Further studies of U oxides, intermediate between UO₂ and UO₃ are in progress.


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.
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$_2$O, which, upon calcination, yields UO$_3$ (amorphous), followed by a solid solution UO$_{2.90}$ (crystalline) then by U$_3$O$_8$ (crystalline); later presents two forms, one susceptible to a reversed process of reoxidation, other nonreoxidable [see Bouille and Domine-Berges, Compt. rend. 227, 1365 (1948); ibid, 228, 72 (1949)].


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$_3$O$_8$, 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$_3$O$_8$ 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$_3$O$_8$ 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.


U-O system is complicated by existence 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.

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


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


From x-ray powder photographs metallic U found to be orthorhombic with \(a:b:c = 2.852 : 5.865 : 4.945\) (kX units), \(Z = 4\) and density calculated at 18.97. Space group is \(V_1^7\) and atoms are in 3 equiv. positions on twofold axes \(Oy_2\), with \(y = 0.105 \pm 0.005\). 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.


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


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.


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, 
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.

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—VANDENBRANDEITE, 
Vandenbrandeite is triclinic with a = 7.84, b = 5.43, c = 6.09 (kX units); α = 91°52', β = 102°00', γ = 89°37' and cell content 2(CuUO₄.2H₂O). 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 ε obtuse, and α < 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, 
UP氮PHERE, KASOLITE AND CUPROSKLODOWSKITE IN CANADA, 
Meta-zeunerite, CaO₂UO₃As₂O₅·12H₂O, 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 occurrence in Canada of mineral. Uranophane, CaU₂Si₂O₇·6H₂O, 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 16, 1899, by Spence, H. S., Am. Mineral. 15, 474 (1930), and by Palache, C. and Berman, H. Am. Mineral. 18, 20 (1933). First occurrence identified by x-rays. Kasolite, PbUSiO₆·H₂O, was noted as orange yellow crusts in association with an unidentified yellow-green radioactive mineral in fractures near center of radioactivity. Microscopic fragments 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. Cupro sklodowskite, CaU₂Si₂O₁₁·6H₂O, is one of the rarest of uranium oxidation products. Mineral was reported only by Vaes, J. P., Ann. Soc. Geol. Belgique 56, Bull. B331 (1935) and by Novacek, P., 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 5UO₃·2SiO₃·6H₂O 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°, α = 1.650, β = 1.685, γ = 1.712, X = c, Y = b, Z = a.
pleochroic, X colorless, Y very pale yellow, Z pale yellow-green; dispersion negligible, in disagreement with previous observations of \( r > \nu \) strong.


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.
<table>
<thead>
<tr>
<th>Author</th>
<th>Page Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alberman, K. B.</td>
<td>45, 452</td>
</tr>
<tr>
<td>Alcock, T. C.</td>
<td>633</td>
</tr>
<tr>
<td>Aloy, F. J.</td>
<td>309, 613, 614</td>
</tr>
<tr>
<td>Amreim, W.</td>
<td>441</td>
</tr>
<tr>
<td>Anderson, J. S.</td>
<td>45, 452, 802</td>
</tr>
<tr>
<td>Andrieux, J. L.</td>
<td>641</td>
</tr>
<tr>
<td>Anonsen, S. H.</td>
<td>445</td>
</tr>
<tr>
<td>Arfvedson, J. A.</td>
<td>401</td>
</tr>
<tr>
<td>Arnott, J. R.</td>
<td>460</td>
</tr>
<tr>
<td>Arden, T. V.</td>
<td>42</td>
</tr>
<tr>
<td>Asbury, I.</td>
<td>328</td>
</tr>
<tr>
<td>Ashman, G. C.</td>
<td>618</td>
</tr>
<tr>
<td>Audrieth, L. F.</td>
<td>722</td>
</tr>
<tr>
<td>Avgustininik, A. I.</td>
<td>723</td>
</tr>
<tr>
<td>Baenziger, N. C.</td>
<td>317, 320, 505</td>
</tr>
<tr>
<td>Balarev, D.</td>
<td>626, 714</td>
</tr>
<tr>
<td>Bassett, L. G.</td>
<td>642</td>
</tr>
<tr>
<td>Beck, G.</td>
<td>718</td>
</tr>
<tr>
<td>Belle, J.</td>
<td>43, 130</td>
</tr>
<tr>
<td>Belov, F. N.</td>
<td>453</td>
</tr>
<tr>
<td>Benson, F. N.</td>
<td>453</td>
</tr>
<tr>
<td>Bernshon, E.</td>
<td>43, 130</td>
</tr>
<tr>
<td>Berzelius, J. J.</td>
<td>1</td>
</tr>
<tr>
<td>Bhattacharyya, R. C.</td>
<td>34</td>
</tr>
<tr>
<td>Billiet, V.</td>
<td>439</td>
</tr>
<tr>
<td>Biltz, W.</td>
<td>627, 712, 717</td>
</tr>
<tr>
<td>Blakey, R. C.</td>
<td>45</td>
</tr>
<tr>
<td>Blum, P.</td>
<td>641</td>
</tr>
<tr>
<td>Bossuet, R.</td>
<td>428</td>
</tr>
<tr>
<td>Boule, A.</td>
<td>464, 640, 725, 727</td>
</tr>
<tr>
<td>Bragdon, R. W.</td>
<td>445</td>
</tr>
<tr>
<td>Brauner, E. B.</td>
<td>702</td>
</tr>
<tr>
<td>Breckpot, R.</td>
<td>321</td>
</tr>
<tr>
<td>Brewer, L.</td>
<td>322, 323, 324, 326, 327, 442</td>
</tr>
<tr>
<td>Bromley, L. A.</td>
<td>322, 324, 327, 442</td>
</tr>
<tr>
<td>Brooker, E. J.</td>
<td>468</td>
</tr>
<tr>
<td>Broy, J.</td>
<td>431</td>
</tr>
<tr>
<td>Brunck, O.</td>
<td>706</td>
</tr>
<tr>
<td>Bucholz, C. F.</td>
<td>400</td>
</tr>
<tr>
<td>Burger, A.</td>
<td>707</td>
</tr>
<tr>
<td>Chaudron, G.</td>
<td>427</td>
</tr>
<tr>
<td>Chiotti, P.</td>
<td>458</td>
</tr>
<tr>
<td>Cline, W. E.</td>
<td>635</td>
</tr>
<tr>
<td>Colani, A.</td>
<td>422</td>
</tr>
<tr>
<td>Colbert, W.</td>
<td>314</td>
</tr>
<tr>
<td>Corwin, R. E.</td>
<td>469</td>
</tr>
<tr>
<td>Cubicciotti, D.</td>
<td>805</td>
</tr>
<tr>
<td>Cay, E. J.</td>
<td>435</td>
</tr>
<tr>
<td>Daane, A. H.</td>
<td>449</td>
</tr>
<tr>
<td>Day, M. J.</td>
<td>643</td>
</tr>
<tr>
<td>Davidson, N. R.</td>
<td>636, 726, 730</td>
</tr>
<tr>
<td>Dieke, G. H.</td>
<td>316</td>
</tr>
<tr>
<td>Ditte, A.</td>
<td>7, 9, 410</td>
</tr>
<tr>
<td>Djatschkowshy, S. J.</td>
<td>436</td>
</tr>
<tr>
<td>Domine-Berges, M.</td>
<td>464, 640, 725, 727, 729</td>
</tr>
<tr>
<td>Donath, J.</td>
<td>604</td>
</tr>
<tr>
<td>Dounce, A. L.</td>
<td>315</td>
</tr>
<tr>
<td>Drenckmann, B.</td>
<td>500</td>
</tr>
<tr>
<td>Duncan, A. B. F.</td>
<td>316</td>
</tr>
<tr>
<td>Duval, C.</td>
<td>639</td>
</tr>
<tr>
<td>Eastman, E. D.</td>
<td>442</td>
</tr>
<tr>
<td>Ebelmen, J. J.</td>
<td>407</td>
</tr>
<tr>
<td>Eckert, A. C.</td>
<td>453</td>
</tr>
<tr>
<td>Egerton, A. C. G.</td>
<td>708</td>
</tr>
<tr>
<td>Eichner, C.</td>
<td>450</td>
</tr>
<tr>
<td>Elsner, L.</td>
<td>701</td>
</tr>
<tr>
<td>Englander, M.</td>
<td>463</td>
</tr>
<tr>
<td>Ertaud, A.</td>
<td>450</td>
</tr>
<tr>
<td>Eyerly, G. B.</td>
<td>469</td>
</tr>
<tr>
<td>Faehr, E.</td>
<td>616</td>
</tr>
<tr>
<td>Fairley, T.</td>
<td>304</td>
</tr>
<tr>
<td>Fendius, C.</td>
<td>717</td>
</tr>
<tr>
<td>Fillmore, C. L.</td>
<td>51, 52, 53, 54, 55</td>
</tr>
<tr>
<td>Fischel, V.</td>
<td>12</td>
</tr>
</tbody>
</table>
Flagg, J. F.—315
Flanders, V. W.—328
Fleischer, M.—332
deforcrand, M.—710
Fowler, G. J.—608
French, C. L.—445
Frers, J. N.—321
Freymann, M.—728
Freymann, R.—728
Fried, S. M.—636, 726, 730
Friederich, E.—433
Fromdel, J. W.—332
Fuyat, B. K.—465
George, D’A.—330
Gibson, G.—333
Gilles, P. W.—322, 323, 327, 442
Gillies, D. M.—634
Giolitti, F.—616
Goldschmidt, B.—454
Goldschmidt, V. M.—430
Gorman, D. H.—808
Grandon, H.—8, 10, 11
Grant, J.—608
Greenwood, H. C.—415
Gronvold, F.—447, 637
Gruen, D. M.—456, 732
Guy-Lussac, T.—600
Hakki, M.—35
Haraldsen, H.—447
Harrison, G. R.—325
Hawk, C. O.—716
Hedvall, J. A.—31, 711
Heidelberger, M.—22
Hermann, H.—409
Hillebrand, W. F.—609
Hodgekisson, W. R. E.—606, 607
Hoekstra, H. R.—41, 49, 731
Hoffman, J. I.—318, 638
Hofmann, K. A.—30, 32
Hogarth, D. D.—807
Holley, C. E.—461
Hoschele, K.—30, 32
Huber, E. J., Jr.—461
Hund, F.—48
Huttig, G. F.—713
Ioffe, A. V.—443
Jacob, C. W.—800
Jary, R.—454, 727
Jolibois, P.—428
Kahn, M.—466
Kargin, V. A.—719, 720
Kassner, O.—14
Katz, J. J.—41, 49, 331, 333, 456, 731, 732, 803
Katzen, L. I.—804
Keller, R.—467
Kelley, K. K.—444, 631
Kent, H., III.—325
Kerr, P. F.—462
Kihlborg, L.—47
Kind, A.—467
Klaproth, M. H.—300
Koehler, W. C.—732
Krause, O.—35
Kreidl, N. J.—314
Kuhn, O. B.—3
Kunheim, H.—603
Lambertson, W. A.—46
Lang, S. M.—51, 52, 53, 54, 55
Larsson, A.—16
Laskin, S.—448
Lauterback, K.—448
Leach, L.—448
Lebeau, P.—429, 709
Lecanu, L. R.—402
Lofgren, N. L.—322, 323, 327, 442
Lorah, J. R.—628
Lories, J.—809
Lowndes, F. K. S.—606, 607
Magneli, A.—47
Mailhe, A.—417
<table>
<thead>
<tr>
<th>Name</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martin, G. L.</td>
<td>445</td>
</tr>
<tr>
<td>McCoy, H. N.</td>
<td>618</td>
</tr>
<tr>
<td>McDonald, R. A.</td>
<td>314</td>
</tr>
<tr>
<td>McGlone, P.</td>
<td>42</td>
</tr>
<tr>
<td>Meierkord, E. H.</td>
<td>461</td>
</tr>
<tr>
<td>Melikoff, P. G.</td>
<td>17, 18, 19, 308</td>
</tr>
<tr>
<td>Metzger, F. J.</td>
<td>22</td>
</tr>
<tr>
<td>Michel, I.</td>
<td>13</td>
</tr>
<tr>
<td>Milne, I. H.</td>
<td>645, 806</td>
</tr>
<tr>
<td>Mixter, W. G.</td>
<td>619</td>
</tr>
<tr>
<td>Mohr, P.</td>
<td>335</td>
</tr>
<tr>
<td>Moissan, H.</td>
<td>610, 612</td>
</tr>
<tr>
<td>Montignie, E.</td>
<td>33</td>
</tr>
<tr>
<td>Moore, G. E.</td>
<td>444</td>
</tr>
<tr>
<td>Mueller, G. W.</td>
<td>437</td>
</tr>
<tr>
<td>Mueller, M. H.</td>
<td>46</td>
</tr>
<tr>
<td>Muller, H.</td>
<td>627</td>
</tr>
<tr>
<td>Murray, P.</td>
<td>459</td>
</tr>
<tr>
<td>Mathmann, W.</td>
<td>306</td>
</tr>
<tr>
<td>Neeb, H. C.</td>
<td>334, 644</td>
</tr>
<tr>
<td>Neogi, P.</td>
<td>34</td>
</tr>
<tr>
<td>Newbery, E.</td>
<td>623</td>
</tr>
<tr>
<td>Nuffield, E. W.</td>
<td>468, 806</td>
</tr>
<tr>
<td>Nichols, E. L.</td>
<td>311</td>
</tr>
<tr>
<td>Oechsner de Coninck</td>
<td>23, 24, 25, 26, 27, 414, 416, 418, 419, 423</td>
</tr>
<tr>
<td>Ortel, Y.</td>
<td>450</td>
</tr>
<tr>
<td>Parera, A.</td>
<td>302</td>
</tr>
<tr>
<td>Parsons, C. L.</td>
<td>426</td>
</tr>
<tr>
<td>Pauling, L.</td>
<td>434</td>
</tr>
<tr>
<td>Peetz, U.</td>
<td>48</td>
</tr>
<tr>
<td>Peiser, H. S.</td>
<td>633</td>
</tr>
<tr>
<td>Peligot, E.</td>
<td>301, 406, 601</td>
</tr>
<tr>
<td>Persoz, J.</td>
<td>2</td>
</tr>
<tr>
<td>Pissarjewsky, L.</td>
<td>17, 18, 19, 20, 308, 310</td>
</tr>
<tr>
<td>Poleck, T.</td>
<td>15</td>
</tr>
<tr>
<td>Priest, G. L.</td>
<td>724</td>
</tr>
<tr>
<td>Priest, H. F.</td>
<td>724</td>
</tr>
<tr>
<td>Prigent, J.</td>
<td>457</td>
</tr>
<tr>
<td>Prigu, J. N.</td>
<td>623</td>
</tr>
<tr>
<td>Rabinowitch, E. I.</td>
<td>331, 803</td>
</tr>
<tr>
<td>Rayner, G.</td>
<td>704</td>
</tr>
<tr>
<td>Raynaud, A.</td>
<td>420, 423, 424</td>
</tr>
<tr>
<td>Hegnault, V.</td>
<td>403, 404</td>
</tr>
<tr>
<td>Reinicke, R.</td>
<td>431</td>
</tr>
<tr>
<td>Remelle, A.</td>
<td>303, 501</td>
</tr>
<tr>
<td>Renz, C.</td>
<td>21</td>
</tr>
<tr>
<td>Richmond, M. S.</td>
<td>329</td>
</tr>
<tr>
<td>Riddle, F. H.</td>
<td>615</td>
</tr>
<tr>
<td>Rideal, E. K.</td>
<td>621, 622</td>
</tr>
<tr>
<td>Rodden, C. J.</td>
<td>329</td>
</tr>
<tr>
<td>Rosenheim, A.</td>
<td>35</td>
</tr>
<tr>
<td>Rosenthal, W.</td>
<td>715</td>
</tr>
<tr>
<td>Roth, R. S.</td>
<td>51, 52, 53, 54, 55</td>
</tr>
<tr>
<td>Rudge, W. A. D.</td>
<td>425</td>
</tr>
<tr>
<td>Rudorff, W.</td>
<td>50</td>
</tr>
<tr>
<td>Rundle, R. E.</td>
<td>317, 320</td>
</tr>
<tr>
<td>Russell, A. S.</td>
<td>620, 625</td>
</tr>
<tr>
<td>Sabatier, P.</td>
<td>307, 412, 413, 417, 502, 705</td>
</tr>
<tr>
<td>Samson, S.</td>
<td>36, 38</td>
</tr>
<tr>
<td>Samsonow, A.</td>
<td>421</td>
</tr>
<tr>
<td>Sanches del Rio, C.</td>
<td>467</td>
</tr>
<tr>
<td>Schmidt, M. T.</td>
<td>722</td>
</tr>
<tr>
<td>Schoop, A.</td>
<td>439</td>
</tr>
<tr>
<td>Schottky, W.</td>
<td>630</td>
</tr>
<tr>
<td>Selwood, P. W.</td>
<td>44</td>
</tr>
<tr>
<td>Senderena, J. B.</td>
<td>305, 412, 413, 502, 705</td>
</tr>
<tr>
<td>Shepardson, J. U.</td>
<td>642</td>
</tr>
<tr>
<td>Shinn, O. L.</td>
<td>411</td>
</tr>
<tr>
<td>Sillen, L. G.</td>
<td>36, 38</td>
</tr>
<tr>
<td>Simon, W.</td>
<td>328</td>
</tr>
<tr>
<td>Sittig, L.</td>
<td>433</td>
</tr>
<tr>
<td>Smith, E. F.</td>
<td>411, 611</td>
</tr>
<tr>
<td>Staehling, C.</td>
<td>503, 504</td>
</tr>
<tr>
<td>Stokland, K.</td>
<td>334, 644</td>
</tr>
<tr>
<td>Last Name</td>
<td>Initials</td>
</tr>
<tr>
<td>-----------</td>
<td>----------</td>
</tr>
<tr>
<td>Stolba</td>
<td>F.-5</td>
</tr>
<tr>
<td>Stohr</td>
<td>J. A.</td>
</tr>
<tr>
<td>Sus</td>
<td>A. N.</td>
</tr>
<tr>
<td>Swanson</td>
<td>H. E.</td>
</tr>
<tr>
<td>Tamman</td>
<td>G.</td>
</tr>
<tr>
<td>Tavanti</td>
<td>G.</td>
</tr>
<tr>
<td>Taylor</td>
<td>N. W.</td>
</tr>
<tr>
<td>Tevebaugh</td>
<td>A. D.</td>
</tr>
<tr>
<td>Tevebaugh</td>
<td>R. D.</td>
</tr>
<tr>
<td>Thomassen</td>
<td>L.</td>
</tr>
<tr>
<td>Tridot</td>
<td>G.</td>
</tr>
<tr>
<td>Trzebiatowski</td>
<td>W.</td>
</tr>
<tr>
<td>Tautsumi</td>
<td>S.</td>
</tr>
<tr>
<td>Uhrlaub</td>
<td>E.</td>
</tr>
<tr>
<td>von Uruh</td>
<td>A.</td>
</tr>
<tr>
<td>Valet</td>
<td>G.</td>
</tr>
<tr>
<td>Van Arkel</td>
<td>A. W.</td>
</tr>
<tr>
<td>Vautrey</td>
<td>L.</td>
</tr>
<tr>
<td>Verdaguer</td>
<td>F.</td>
</tr>
<tr>
<td>Wagner</td>
<td>C.</td>
</tr>
<tr>
<td>Wamsler</td>
<td>C. A.</td>
</tr>
<tr>
<td>Warf</td>
<td>J. C.</td>
</tr>
<tr>
<td>Warren</td>
<td>B. E.</td>
</tr>
<tr>
<td>von Wartenberg</td>
<td>H.</td>
</tr>
<tr>
<td>Watts</td>
<td>J. I.</td>
</tr>
<tr>
<td>Wertheim</td>
<td>I.</td>
</tr>
<tr>
<td>Werther</td>
<td>G.</td>
</tr>
<tr>
<td>Wiberley</td>
<td>S. E.</td>
</tr>
<tr>
<td>Widdowson</td>
<td>W. P.</td>
</tr>
<tr>
<td>Wilber</td>
<td>D. T.</td>
</tr>
<tr>
<td>Wilhelm</td>
<td>H. A.</td>
</tr>
<tr>
<td>Wilke-Dorfurt</td>
<td>E.</td>
</tr>
<tr>
<td>Williamson</td>
<td>B.</td>
</tr>
<tr>
<td>Wilson</td>
<td>A. S.</td>
</tr>
<tr>
<td>Wohler</td>
<td>F.</td>
</tr>
<tr>
<td>Yant</td>
<td>W. P.</td>
</tr>
<tr>
<td>Zachariasen</td>
<td>W. H.</td>
</tr>
<tr>
<td>Zahn</td>
<td>L. G.</td>
</tr>
<tr>
<td>Zimmermann</td>
<td>J. L. C.</td>
</tr>
<tr>
<td>von Zweigbergk</td>
<td>N.</td>
</tr>
</tbody>
</table>
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 Scandinaavica
Am. J. Sci. — American Journal of Science
Am. Mineral. — American Mineralogist
Ann. — Annalen der Chemie
Ann. chim. — Annales de Chimie
Ann. chim. phys. — Annales de chimie et de physique
Arch. Pharm. — Archiv der Pharmazie
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, Academia 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
Compt. rend. — Comptes rendus hebdomadaires des seances de l'academie des sciences
Gazz. chim. ital. — Gazzetta chimica italiana
Geol. Foren. i Stockholm Forh. — Geologiska Foreningens i Stockholm Forhandlingar
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

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>442</td>
<td>1899</td>
<td>326</td>
<td>AECD-1294</td>
<td>461</td>
</tr>
<tr>
<td>442</td>
<td>315</td>
<td>2244</td>
<td>448</td>
<td>AEERE-M/R-507</td>
<td>459</td>
</tr>
<tr>
<td>609</td>
<td>724</td>
<td>2581</td>
<td>453</td>
<td>BR-50</td>
<td>319</td>
</tr>
<tr>
<td>647</td>
<td>634</td>
<td>2624</td>
<td>803</td>
<td>BR-589</td>
<td>633</td>
</tr>
<tr>
<td>688</td>
<td>316</td>
<td>2647</td>
<td>41</td>
<td>CEA-35</td>
<td>450</td>
</tr>
<tr>
<td>777</td>
<td>318</td>
<td>2652</td>
<td>328</td>
<td>CEA-79</td>
<td>463</td>
</tr>
<tr>
<td>1152</td>
<td>37</td>
<td>2667</td>
<td>331</td>
<td>GS-C-74</td>
<td>332</td>
</tr>
<tr>
<td>1242</td>
<td>322</td>
<td>2877</td>
<td>333</td>
<td>NYOO-98</td>
<td>642</td>
</tr>
<tr>
<td>1273</td>
<td>320</td>
<td>2933</td>
<td>43</td>
<td>RMO-563</td>
<td>330</td>
</tr>
<tr>
<td>1435</td>
<td>445</td>
<td>2954</td>
<td>731</td>
<td>RMO-715</td>
<td>462</td>
</tr>
<tr>
<td>1499</td>
<td>446</td>
<td>3068</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1526</td>
<td>635</td>
<td>3204</td>
<td>458</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1543</td>
<td>323</td>
<td>3237</td>
<td>505</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1581</td>
<td>325</td>
<td>3316</td>
<td>329</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1659</td>
<td>636</td>
<td>3349</td>
<td>469</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1722</td>
<td>324</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(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:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MDDC-758</td>
<td>444</td>
<td>MDDC-1608</td>
<td>317</td>
</tr>
<tr>
<td>MDDC-1242</td>
<td>327</td>
<td>AECD-2139</td>
<td>39</td>
</tr>
<tr>
<td>MDDC-1543</td>
<td>327</td>
<td>NP-3208</td>
<td>805</td>
</tr>
<tr>
<td>MDDC-1572</td>
<td>801</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### (c) Listing of AEC Reports Given by Title Only

<table>
<thead>
<tr>
<th>Report</th>
<th>Group</th>
<th>Report</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDDC-279</td>
<td>U-oxides, general</td>
<td>MDDC-1725</td>
<td>U-oxides, general</td>
</tr>
<tr>
<td>MDDC-366</td>
<td>U-oxides, general</td>
<td>AECD-1988</td>
<td>U-oxides, general</td>
</tr>
<tr>
<td>MDDC-467</td>
<td>U-oxides, general</td>
<td>AECD-2307</td>
<td>U-oxides, general</td>
</tr>
<tr>
<td>MDDC-901</td>
<td>$\text{U}_3\text{O}_8$</td>
<td>AECD-2740</td>
<td>$\text{UO}_3$</td>
</tr>
<tr>
<td>MDDC-911</td>
<td>$\text{UO}_3$</td>
<td>AECD-2819</td>
<td>U-oxides, general</td>
</tr>
<tr>
<td>MDDC-1564</td>
<td>$\text{U}_3\text{O}_8$</td>
<td>NP-1602</td>
<td>$\text{U}_3\text{O}_8$</td>
</tr>
</tbody>
</table>

U.S. GOVERNMENT PRINTING OFFICE 5-1952