

INVESTIGATION OF URANIUM OXIDE OF
LOW OXIDATION STATE

by

CARL W. NELSON

Carl W. Nelson
Department of Chemistry
Massachusetts Institute of Technology

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Signature of Author.....
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Signature of Professor
in Charge of Research....

Signature of Head of Department.. .

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ABSTRACT

An investigation was undertaken to determine the oxidation state of uranium in the black solid formed in the electrolytic reduction of uranyl chloride in hydrochloric acid and from the reaction of uranium metal with hydrochloric acid. Past investigators considered the black solid to have the formula UO_2 . However, their analyses were performed in the presence of air. The analyses reported in this thesis were carried out in the absence of air. Two runs where significant amounts of the oxide were collected indicate an oxidation state for uranium of 1.987 and 2.270 respectively. It is the opinion of the author that the colloidal black oxide which is formed has the formula UO . More work is necessary to confirm these results.

I. INTRODUCTION

The element uranium on the basis of chemical evidence is better placed with chromium, molybdenum, and tungsten in Group VI-A of the periodic system than as a member of a 5f inner transition series analogous to the 4f rare earth series. Uranium shows the same numerous oxidation states as the other members of the group. Oxidation states of +3, +4, +5, and +6 are known for uranium. Tungsten and molybdenum form compounds having the positive oxidation states 2,3,4,5, and 6, while chromium forms compounds in which it has the oxidation numbers +2,+3, and +6. Thus, uranium, especially in that it is easily oxidized to the +6 state, strongly resembles chemically the other elements of Group VI-A.

(1)
Oxidation states for uranium of +3, +4, +5, and +6 are represented in the halides and in the ions U^{+3} , U^{+4} , UO_2^{+2} , and UO_2^{+4} . However, only the +4 and +6 states are stable in aqueous solution. The trichloride and pentachloride may be prepared at high temperatures, but the former is oxidized by water with the evolution of hydrogen, and the latter decomposes in water into compounds of the +4 and +6 states. The ion U^{+3} forms an intense red solution, but is oxidized by water with the evolution of hydrogen at an appreciable rate. It is said that strong hydrochloric acid stabilizes the solution. Solutions of U^{+4} are green in color, and UO_2^{+4} solutions, yellow.

The three oxides UO_2 , U_3O_8 , and UO_3 are well known. UO_2 and UO_3 may be prepared from aqueous solution and U_3O_8 upon ignition. The colors given in the literature for these oxides are many and

apparently depend on the method of preparation. In addition to these oxides there are known to exist the monoxide UO , and the oxide U_2O_5 . These have been prepared in the dry way.

The oxygen (2)(3) chemistry of uranium is interesting because of the complex phase relationships in the uranium—oxygen system. Since solid solutions are readily formed, it is possible to obtain uranium oxides in the dry way with practically any composition between UO and UO_3 and with many crystal structures. The monoxide, UO , has a rock-salt structure and because of its semi-metallic nature, i.e., its relatively high electronic conductivity, it is regarded as an interstitial compound.

In this thesis a compound of uranium which exhibits a formal valency of +2 (or at least of lower than +3) has been prepared from aqueous solution. The compound has been assigned the formula UO .

The uranium oxide whose oxidation state is less than +3 may be prepared by two methods: (1) by reaction of uranium metal with hydrochloric acid, and (2) by electrolytic reduction of uranyl chloride in hydrochloric acid. The preparations must be carried out in the absence of air.

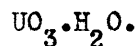
Extensive studies of the chemistry of uranium were undertaken during World War II and later by the Atomic Energy Commission. (1)(4) In the course of their work it was learned that a black solid and a red solution, which on standing is changed to green, are formed when uranium metal is reacted with hydrochloric acid. However, the black solid was not analyzed in the absence of air in these investigations.

(5)

A. Samsonoff in 1911 prepared the black solid by electrolyzing a solution of uranyl chloride. He considered the compound to be UO_2 and reported that it appears as a black colloidal substance in the cathode compartment of the cell. He claimed that the substance is soluble in water, giving a dark-colored solution which shows the presence of ultramicroscopic particles. The same substance, he reported, is also obtained in the reduction of UO_2Cl_2 by zinc and hydrochloric acid. In this preparation, he noticed that UCl_4 acts as a protector and increases the stability of the colloidal solution.

(5)

C.E. Pierle in 1919 regarded the black substance formed on electrolyzing an aqueous solution of a uranyl salt to be



The work reported in this thesis indicates that the formal valency of uranium in the black colloidal compound whether formed by the reaction of uranium metal in hydrochloric acid or by the electrolytic reduction of UO_2Cl_2 in hydrochloric acid is lower than +3 and probably +2.

II. THE ELECTROLYTIC REDUCTION OF URANIUM (VI) IN AQUEOUS SOLUTION

The method was originally described by A. Rosenheim and H. Löbel⁽⁷⁾ in 1908. They prepared a solution of the trichloride in a large excess of hydrochloric acid by the electrolytic reduction of a solution of UO_3 in hydrochloric acid of specific gravity 1.12 (12N), using a layer of mercury as the cathode. Later A. Samsonoff⁽⁵⁾ used the same method to prepare what he considered to be colloidal UO_2 . C.E. Pierle⁽⁶⁾ thought the substance formed on electrolysis to be $UO_3 \cdot H_2O$.

The apparatus that was employed for work reported in this thesis is similar in design to the original one of A. Rosenheim and H. Löbel⁽⁷⁾.

The cell (Figure I), prepared from a 500 ml. Erlenmeyer flask, consists of a large cathode chamber (A), into which is set a porous cup (B) for the anode compartment. The anode is a carbon rod (C) and the cathode is a pool of mercury (D) on the bottom of the cell to which contact is made by a platinum wire (E).

Two tubes extend from the anode compartment, one (F) for filling the cup, and the other (G) for allowing the escape of the gas generated by the reaction. From the cathode section, three tubes extend, one (H) for the cathode wire, the second (I) for filling the cell and for passing into the cell the inert gas, and the third (J) for the escape of the gas. The cell is sealed, except for the openings, with sealing wax.

In all runs, the anode compartment was filled with hydrochloric acid to a volume of 40 ml. Carbon dioxide gas was passed through the cathode section to stir the solution, to provide an

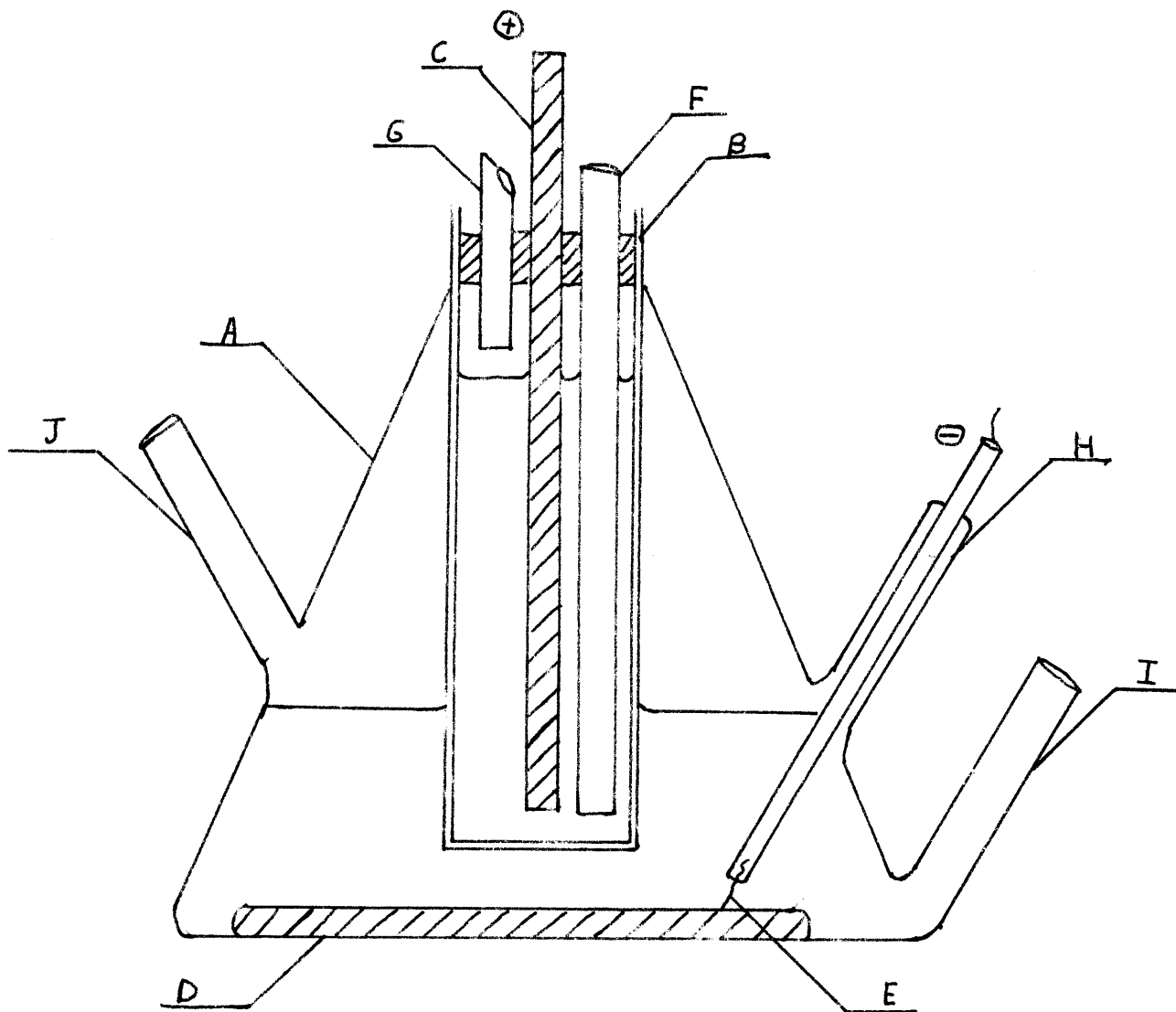


FIGURE I

The Electrolytic Cell

- | | |
|--------------------------------|-----------------------|
| A - cathode chamber | F - filling tube |
| B - anode chamber (porous cup) | G - outlet tube |
| C - carbon anode | H - cathode wire tube |
| D - mercury cathode | I - filling tube |
| E - platinum contact wire | J - outlet tube |

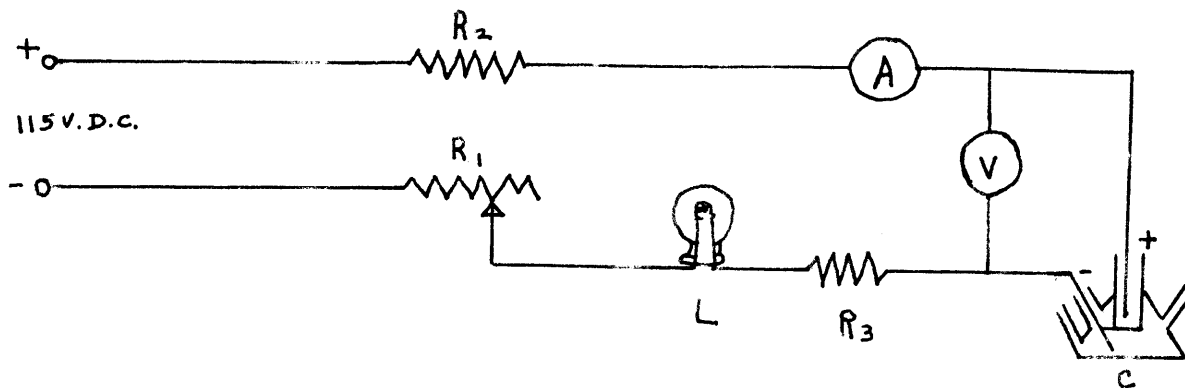


FIGURE II

Electrical Circuit

R_1 - Variable Resistor

R_2, R_3 - Fixed Resistance

L - 150 Watt Light Bulb

A - Weston Ammeter

V - Weston Voltmeter

C - Electrolytic Cell

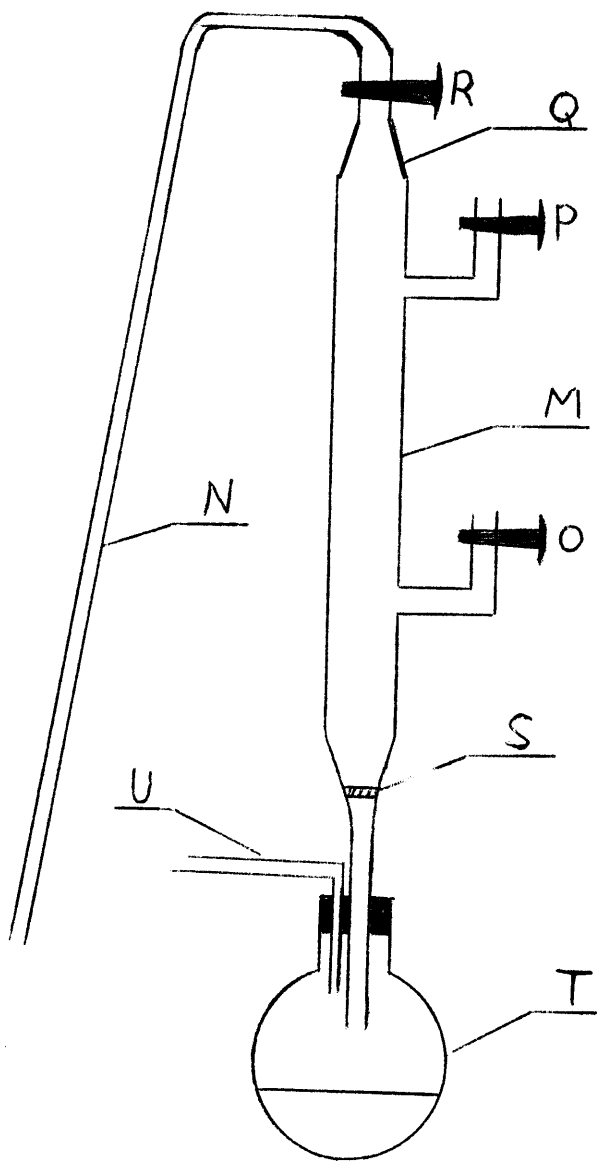


FIG III

inert atmosphere over the solution, and to sweep out the hydrogen gas formed during the reaction. In order to prevent the escape of chlorine gas into the atmosphere, a trap was connected to the outlet tube from the anode compartment.

The electrical circuit for the cell is as shown in Figure II. The 115 volt D.C. supply was reduced by several resistors including a variable resistor and a 150 watt light bulb. The cell was operated at a current of 0.4 to 0.8 amperes. The potential across the cell varied from 2.0 to 4.0 volts.

The apparatus for collecting the colloidal black oxide formed at the cathode is illustrated in Figure III. The tube (M) is about 2 cm. in diameter and 50 cm. in length. At position (O) and (P) are right angle side arms with stopcocks. The section containing stopcocks (R) is fitted to tube (M) at the ground glass joint (Q). The delivery tube (N) which is used to convey the solution and solid from tube (I) of the cell to tube (M) is attached to the section containing stopcock (R). At the bottom of tube (M) is a fritted glass filter plate (S) whose tube extends into flask (T) to which suction may be applied at (U).

In all runs the apparatus was flushed with prepuried nitrogen to remove the air before delivery of the material from the cell. After the solution and solid from the cell had been conveyed to tube (M) a nitrogen atmosphere was kept over the solution by passing nitrogen through stopcock (P) and out stopcock (R). After the solution had filtered through to flask (T) whether by suction or by time the black solid remaining on the glass wool or absorbent over the fritted glass filter glass could be washed with acid and oxidized ^{6N H₂SO₄}

by ceric ammonium sulfate from the inlet at stopcock (O).

All of the runs made with the cell involved the electrolytic reduction of uranyl chloride in hydrochloric acid. The concentrations of uranyl chloride and hydrochloric acid were varied for the runs.

In the first two runs four grams (0.01114 moles) of UO_2Cl_2 was dissolved in 75 ml. of 6 N HCl, and this solution was placed in the cathode section of the cell. The electrolyses were run for four and twenty hours respectively at a current of 0.8 amperes. The potential across the cell was noted to increase from 3.0 to 4.0 volts during the runs. The solution changed in color from yellow of UO_2^{++} ion to green of U^{+4} ion, and finally to dark red of U^{+3} ion. The dark red solution showed the presence of colloidal ultramicroscopic particles, first seen by A. Samsonoff.

The solution from the cell was ~~siphoned~~ ^{transferred by suction} into the apparatus illustrated in Figure III and described above. The solution remained dark red in color with the finely divided particles suspended in it. From the solution hydrogen gas was evolved. The solution was allowed to stand three days in the apparatus with a nitrogen atmosphere. While standing the solution changed in color from dark red to dark green, and continued to show the presence of the colloidal substance. Hydrogen gas still evolved after three days of standing.

The solution was filtered through the glass wool and the fritted glass disk, the last going through so slowly it was filtered by suction. The very small amount of black solid that remained on the glass wool was washed with $6\text{NH}_2\text{SO}_4$. To determine

the oxidation state of uranium in the black solid, a volume of 10.00 ml. of standardized ceric ammonium sulfate solution was added. This was back titrated to the end point with standardized ferrous ammonium sulfate solution. The potassium salt of diphenylamine sulfonic acid was used as an indicator.

To determine the amount of uranium present in the black solid, following the titration, the solution was passed through a Jones reductor, aerated to oxidize any U^{+3} ion formed, and titrated with the standardized ceric ammonium sulfate solution. The same volume of ferrous ammonium sulfate solution that was used as a back titrant in the first titration was passed through the Jones reductor, aerated for five minutes, and titrated with the standardized ceric ammonium sulfate solution. This volume was subtracted from that used in titrating both the U^{+4} and Fe^{+2} from the Jones reductor. This procedure was followed for all the analyses.

By this method of analysis 0.0015g. of uranium was found and its oxidation state in the black solid was +3.761 for the second run. Since the amount of uranium collected was so small, this result was regarded as insignificant.

The third run was carried out in 3NHCl using 7.1 grams (0.01977 moles) of UO_2Cl_2 . The electrolysis was run for twenty-four hours as before. The oxidation state for the uranium was determined to be 1.81 and 0.0024 g. of uranium was found. Again, the result was considered to be insignificant because of the very small amount of uranium.

It was thought that the colloidal uranium oxide could be absorbed on some material so that more of it could be collected.

Some aluminum oxide, which was at hand, was placed on the fritted glass filter plate in the filtering apparatus. The solution from the fourth electrolysis run in 3NHCl was passed through the aluminum oxide. The solution appeared to filter clearer than ever before and the aluminum oxide became darker. This indicated that the aluminum oxide was absorbing the black colloidal uranium oxide. Since the aluminum oxide that was used contained iron the results for this run were meaningless. This run did demonstrate the effectiveness of an absorbent, however.

The fifth electrolysis was run for twenty-four hours. Six grams (0.01671 moles) of UO_2Cl_2 in 3NHCl was used. Iron free silica gel was substituted for the aluminum oxide in the filtering apparatus. When the solution from the cell came in contact with the silica gel heat was developed. The air contained in the silica gel seemed to have oxidized the colloidal uranium oxide. The analytical results showed that the air from the silica gel had oxidized the colloidal oxide, for the oxidation state of uranium was 3.788. The silica gel had absorbed 0.0734 g. of uranium.

In the following run, during the electrolysis most of the solution from the cell was lost. More solution was added and the electrolysis was allowed to continue for three and one-half hours. This run contained the same concentrations of UO_2Cl_2 and HCl as the previous one. Air was removed from the silica gel in the filtering apparatus by wetting it with HCl. An oxidation state of 1.651 was determined for the uranium in the colloidal oxide and 0.0133 g. of uranium was collected.

Unfortunately, in the next run difficulty was experienced in

the transfer of the solution from the cell to the filtering apparatus. Mercury from the cell was carried along. In the last run some of the measured volume of the standard ceric solution was lost so that a determination could not be made. The electrolysis in the last run was carried out with a current of 0.4 ampere instead of the usual 0.8 ampere. It was noticed that although the solution became dark red in color there were hardly any suspended particles in the solution. Consequently, a current of 0.8 ampere is needed to reduce the uranium to an oxidation state of less than +3, so that the colloidal uranium oxide may be formed.

In another experiment it was found that for the most part the particles are less than one micron in size. A fritted glass filter plate whose pore size was one micron was used to establish this fact. Most of the particles passed through the ultra-fine filter.

III. THE REACTION OF URANIUM METAL WITH HYDROCHLORIC ACID

Two determinations of the black colloidal oxide formed from the reaction of uranium metal with hydrochloric acid were made. The apparatus used for collecting the colloid is illustrated in Figure III and described in the previous section of this thesis. Silica gel from which the air had been removed was the absorbent that was used.

In the first determination 0.4391 g. of polished uranium metal was dissolved in 12 ml. of 1.5 N HCl through which nitrogen had been passed to remove the dissolved air. The reaction was carried out in the filtering apparatus with a nitrogen atmosphere. The uranium in the black colloidal oxide indicated a formal valency of 1.987. An amount of 0.0508 g. of uranium was found.

In the second determination an oxidation state of 2.270 was determined for uranium in the black solid and 0.1034 g. of uranium was collected. This reaction employed 1.1155 g. of uranium metal in 15 ml. of 6N HCl.

IV. SUGGESTIONS FOR FURTHER RESEARCH

A. The filtering apparatus may be improved so as to eliminate the possibility of the diffusion of air upwards from the flask through the filter to the solution.

B. The use of an absorbent for the colloidal uranium oxide is promising. Chemically pure refractory oxides, such as aluminum oxide for chromatographic purposes, ought to be tried. The experiments with silica gel should be continued.

C. A comparison of the properties of the colloidal uranium oxide with that of uranium monoxide prepared in the dry way should be made. This can be done providing a sufficient amount of the colloid can be collected.

D. It would be interesting to carry out the same experiments with the uranides, neptunium, plutonium, and americium. The chemistry of these elements is similar to that of uranium. The only divalent form known for these elements are their monoxides NpO , PuO , and AmO , all of which have metallic properties. Perhaps these oxides could be prepared by the electrolytic reduction in aqueous solution of salts of these elements or by the reaction of the metals with hydrochloric acid in the absence of air. The reduction ought to be easier with increasing atomic number of these elements.

Work of this kind on these elements would contribute more chemical evidence to Dr. Coryell's ⁽⁸⁾ contention leading to the designation of these elements as uranides, having the characteristics of a 6d transition group rather than as members of a 5f

inner transition series.

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