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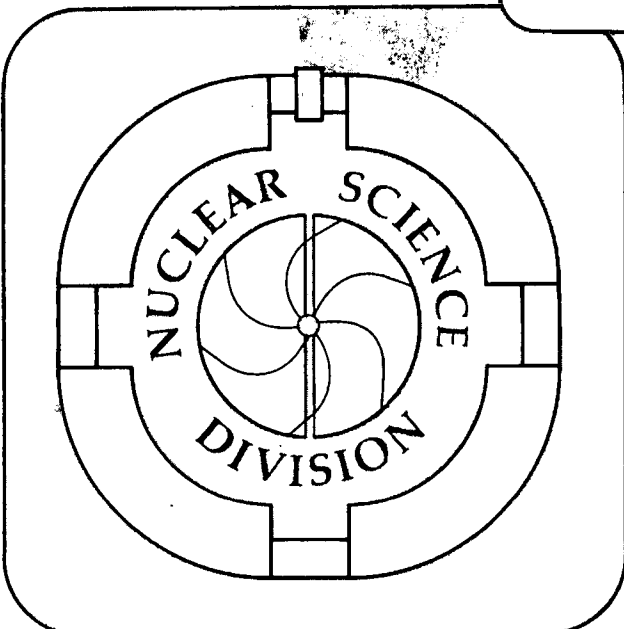
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FORTY YEARS OF PLUTONIUM CHEMISTRY: THE BEGINNINGS

Glenn T. Seaborg

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FORTY YEARS OF PLUTONIUM CHEMISTRY: THE BEGINNINGS

Glenn T. Seaborg

Lawrence Berkeley Laboratory
and Department of Chemistry
University of California
Berkeley, CA 94720

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October 11, 1982

The first isolation of a chemical compound of plutonium (a fluoride) took place on August 20, 1942 and the first weighing of a pure compound (2.77 micrograms of the dioxide) on September 10, 1942. Thus this Symposium marks quite precisely the 40th anniversary of these events, the beginnings of the investigation of the macroscopic (non-tracer) chemical properties of this important synthetic element. The immediately following ultramicrochemical studies led to a definition of the IV and VI oxidation states, some properties of the metallic state, the synthesis and characterization of numerous solid compounds and the crucial testing of the first method devised for its separation and isolation in pure form after its production in the nuclear chain reaction. Later work with larger amounts, available as the result of its production in a nuclear reactor, made it possible to characterize the III and V oxidation states and many more compounds.

Introduction

The last forty years have seen an extensive, world-wide investigation of the chemical properties of the synthetic element, plutonium. As a result, as much is known about the chemical properties of this element as is known about the chemical properties of most of the naturally occurring elements. The papers in this volume, presented at the Symposium on the Chemistry of Plutonium held during the Kansas City meeting of the American Chemical Society, in September, 1982, represent an up-dating of this large amount of information.

In the time and space available to me, I shall largely confine my comments to the origin of the chemical studies on this remarkable element. In so doing I shall include quotations from my Journal in order to help capture some of the flavor of this pioneering work.

The first isolation of a chemical compound of plutonium (a fluoride) took place on August 20, 1942 and the first weighing of a pure compound (2.77 micrograms of the dioxide) on September 20, 1942 at the wartime Metallurgical Laboratory of the University of Chicago. These events represent the beginning of the investigation of the macroscopic (non-tracer) chemical properties of plutonium and this Symposium corresponds quite precisely to the 40th anniversary of these inaugural experiments.

Tracer Chemical Investigations at Berkeley

Tracer investigations during 1941 and early 1942 at Berkeley led to a great deal of information about the chemical properties of plutonium. It was learned that it has at least two oxidation states, the higher of which is not carried by lanthanum fluoride or cerium fluoride, while the lower state is quantitatively coprecipitated with these compounds. It was established that the higher oxidation state can be obtained by treatment of the lower state with oxidizing agents such as persulfate and argentic ions, dichromate, permanganate, or periodate, and that the upper state can be reduced to a lower (rare earth fluoride-carriable) state by treatment with sulfur

dioxide or bromide ion. The approximate potential of the couple plutonium (reduced)→plutonium (oxidized) was believed to be between -1.0 and -1.4 volts. It was established that plutonium in aqueous solution is not reduced to the metal by zinc, and that it does not form a volatile tetroxide. It was shown that a stable lower state of plutonium--probably plutonium (IV)--is carried by $\text{Th}(\text{IO}_3)_4$. Ether extraction was used to separate large amounts of uranyl nitrate from plutonium. Methods also were devised for the separation of plutonium from elements 90, 91, and 93.

On the basis of these facts, it was speculated that plutonium in its highest oxidation state is similar to uranium (VI) and in a lower state is similar to thorium (IV) and uranium (IV). It was reasoned that if plutonium existed normally as a stable plutonium (IV) ion, it would probably form insoluble compounds or stable complex ions analogous to those of similar ions, and that it would be desirable (as soon as sufficient plutonium became available) to determine the solubilities of such compounds as the fluoride, oxalate, phosphate, iodate, and peroxide. Such data were needed to confirm deductions based on the tracer experiments.

When the Plutonium Project was established early in 1942, for the purpose of producing plutonium via the nuclear chain reaction in uranium in sufficient quantities for its use as a nuclear explosive, we were given the challenge of developing a chemical method for separating and isolating it from the uranium and fission products. We had already conceived the

principle of the oxidation-reduction cycle, which became the basis for such a separations process. This principle applied to any process involving the use of a substance which carried plutonium in one of its oxidation states but not in another. By use of this principle, for example, a carrier could be used to carry plutonium in one oxidation state and thus to separate it from uranium and the fission products. Then the carrier and the plutonium could be dissolved, the oxidation state of the plutonium changed, and the carrier precipitated again, leaving the plutonium in solution. The oxidation state of the plutonium could again be changed and the cycles repeated. With this type of procedure, only a contaminating element having a chemistry nearly identical with plutonium would fail to separate if a number of oxidation-reduction cycles were employed. This principle, of course, applies to other types of processes, such as volatility, solvent extraction, or adsorption methods.

Move to Metallurgical Laboratory

The work on the Plutonium Project in early 1942 was centralized in the Metallurgical Laboratory of the University of Chicago. The following extract from my journal describes my arrival in Chicago with my colleague Isadore Perlman:

Sunday, April 19, 1942

This morning at 9:30 a.m. Isadore Perlman and I arrived in Chicago aboard the City of San Francisco. Although our trip from Berkeley took almost two full

days, we feel that the time has not been wasted. Many lively discussions ensued in the privacy of our bedroom and, with appropriate care, in the club car regarding ways to separate element 94 chemically from uranium (that will be neutron-irradiated in chain-reacting piles) and from the fission by-products that will be produced concurrently in the neutron-irradiation process. This overall problem of element 94 isolation will occupy most of our attention for some time to come. The work of my group in the Department of Chemistry at the University of California, Berkeley, during the period August 1940 to the present, has produced much of the background information which is the basis of the Metallurgical Project. (This is the code name for the project whose mission is to produce fissionable element 94 in sufficient quantity for use in a nuclear weapon, and the project is centered at the University of Chicago.)

Our research at Berkeley has resulted in the discovery of element 94, demonstration of the slow neutron fissionability of its isotope 94^{239} , discovery and demonstration of the slow neutron fissionability of U^{233} , spontaneous fission measurements on these isotopes, discovery of 93^{237} , isolation of and nuclear measurements on U^{234} , study of the chemical properties and methods of chemical separation and isolation of element 94, demonstration of the presence of small concentrations of 94 in nature and much related information.

I have known Perlman since our undergraduate days at UCLA. When I went to Berkeley to begin my graduate work, he also transferred to Berkeley to complete his work for a B.S. degree in chemistry. He later obtained his Ph.D. in physiology at Berkeley and after some postdoctoral work there joined my group in January and soon became a key man in this effort.

When we stepped into the street from the Chicago and Northwestern Railroad Station at Canal and Madison Streets the temperature was a cold 40° F, a rather sharp contrast to that in Berkeley when we left. Staring us in the face was the headline in the Chicago Sun, "Tokyo Fears New Bombings; Reports Fires in Four Cities" with sub-heads "Five-Hour Raid on Japanese Laid to Yanks" and "Capital, Yokohama, Kobe and Nagoya Blasted." The account went on to say, "Earlier Japanese broadcasts said attacks, which began at noon yesterday, were carried out by high-flying United States planes which swept in from several directions and started fires among the flimsy wood and paper homes of the heavily populated areas," and continued with, "Neither Washington nor General Douglas MacArthur's headquarters of the United Nations forces in Australia would say that Japan has been attacked by air."

We took a cab from the station to the Shoreland Hotel (55th Street at Lake Michigan) near the University of Chicago campus. We registered here and about noon returned to the downtown area via the Illinois Central commuter line.

Following lunch we attended the Chicago Theater for a Sunday matinee and saw a stage show featuring Kay Kayser's band and a movie, "Design for Scandal," with Walter Pidgeon. We had dinner, returned here to our hotel, after which I wrote to Helen, my bride-to-be.

This day marks my 30th birthday and a transition point in my life, for tomorrow I will take on the added responsibility of the 94 chemistry group at the Metallurgical Laboratory on the University of Chicago campus, the central component of the Metallurgical Project.

We went to work immediately. Other chemists were added to my group and before the end of the month we were assigned space in and moved to the area on the fourth floor of George Herbert Jones Laboratory on the University of Chicago campus (Fig. 1).

Although the outline of a chemical separation process could be obtained by tracer-scale investigations, the process could not be defined with certainty until study of it was possible at the actual separation plants. Therefore, the question in the summer of 1942, was as follows: How could any separations process be tested at the concentrations of plutonium that would exist several years later in the production plants when, at this time, there was not even a microgram of plutonium available? This problem was solved through an unprecedented series of experiments encompassing two major objectives. First, it was decided to attempt the production of an actually weighable amount of plutonium by bombarding large amounts of uranium with

the neutrons from cyclotrons. It must be remembered that never before had weighable amounts of transmutation products been produced with any particle acceleration machine. Even extending this possibility to the limit, it was not anticipated that more than a few micrograms of plutonium could be produced. The second aspect of the solution of this problem involved the novel idea of attempting to work with only microgram amounts of plutonium but, at the same time, at ordinary concentrations. It was decided to undertake a program of investigation involving volumes of solutions and weighings on a scale of operations much below that of ordinary microchemistry.

We solved the first problem by bombarding large amounts of uranyl nitrate with neutrons at the cyclotrons at the University of California and Washington University; plutonium concentrates were derived from these sources through the efforts of teams of chemists who used ether extractions to separate the bulk of the uranium and an oxidation-reduction cycle with rare earth fluoride carrier to concentrate the product. I managed to convince chemists trained in the techniques of ultramicrochemistry to join us to solve the second problem--Burris B. Cunningham and Louis B. Werner of the University of California and Michael Cefola from New York University

Isolation of Plutonium

The first isolation of plutonium was effected in room 405, Jones Laboratory, by starting with a concentrate containing the order of a microgram of plutonium in about 10 milligrams of

rare earths prepared for us by Arthur C. Wahl and co-workers at Berkeley. My journal records this event as follows:

Thursday, August 20, 1942

Perhaps today was the most exciting and thrilling day I have experienced since coming to the Met Lab. Our microchemists isolated pure element 94 for the first time! This morning Cunningham and Werner set about fuming (with evolution of SO_3) yesterday's 94 solution containing about one microgram of 94^{239} , added hydrofluoric acid whereupon the reduced 94 precipitated as the fluoride, or perhaps a double fluoride, free of carrier material, from a total solution volume of 15 cubic millimeters.

This precipitate of 94, which was viewed under the microscope and which was also visible to the naked eye, did not differ visibly from the rare-earth fluorides. (Shortly after the 94 was precipitated, a considerable amount of K_2SiF_6 was observed to separate, as a result of the fact that precipitation had been performed in glass vessels. This will be avoidable in future work because we ^{have} now developed suitable fluoride-resistant micro vessels.)

From the alpha-activity remaining in the supernatant liquid after the final precipitation as a fluoride, it can be calculated, using 30,000 years as the half-life of 94^{239} , that this salt of 94 has a solubility of the order of magnitude of 10 mg of the element per liter of 6 N HF solution. This value is necessarily somewhat tentative.

By afternoon a holiday spirit prevailed in our group.

Covey brought in photo floodlamps and his 35 mm camera and photographed everything in sight (Figs. 2 and 3). By this time the precipitated 94 fluoride had taken on a pinkish hue. Perlman, Cefola and I, and many others, including Kohman, Jaffey and their helpers, who were working in the attic laboratory on the extraction of 94^{239} from neutron-bombarded UNH, came into Room 405 to peer through the microscope at the tiny speck.

All this while, Kohman, Jaffey and their assistants were recrystallizing the UNH from the first ether extraction, which they have been doing for the last two days. In this step, the four separate solutions were taken to the roof and transferred into 14-inch evaporating dishes, set over hot plates, and heated to almost boiling. Each concentrate was kept simmering; and, as it thickened from evaporation, it was vigorously stirred. When it was evident that there remained a ratio of $6H_2O$ to one uranium nitrate by the porcelain chip test, the heating was stopped. Stirring continued, however, until the mass cooled down and hexahydrate crystals appeared. Each dish was weighed before and after emptying. The total net weight of the reconstituted UNH crystals containing the 93 and 94 is 31 lb., 10.5 oz.

The last paragraph in this extract refers to work on the separation of uranium by ether extraction as a step ^{toward} obtaining a plutonium concentrate from a large sample of neutron-irradiated uranyl nitrate.

First Weighing of Plutonium

The first weighing of a pure plutonium compound is described in the following extract from my journal:

Thursday, September 10, 1942

During the last couple of days Cunningham and Werner have been working to establish the degree of purity of the precipitate of 94 oxide that they weighed on Monday. When the 94 oxide was dissolved off the platinum weighing boat with H_2SO_4 , they oxidized with $\text{S}_2\text{O}_8^{-2} + \text{Ag}^{+2}$, followed by the addition of HF; unfortunately a precipitate appeared which must be caused by unremoved La^{+3} . This indicated that something has been holding back some La^{+3} during the LaF_3 precipitations; this led Cunningham and Werner to make an investigation of this phenomenon through the use of tracer experiments with radioactive lanthanum fission product. From these experiments they were able to conclude that the concentration of HNO_3 must be about 1 M (the concentration had been higher in their experiments) in order to insure the complete precipitation of the lanthanum fluoride from the $\text{S}_2\text{O}_8^{-2} + \text{Ag}^{+2}$ solution. They also concluded this oxidizing agent is perhaps the best to use in the oxidation-reduction cycles. Although they have been unsuccessful so far in isolating pure 94, they feel that they have now established the procedures for doing so.

Thus prepared, today Cunningham and Werner are

tackling experiments with Kohman's cleaner one-fourth portion (batch no. 2) of 94^{239} isolated from the large St. Louis bombardment of UNH with cyclotron neutrons. According to Kohman's analysis, this solution contains about 8×10^6 alpha particle disintegrations per minute, corresponding to about 70 micrograms of 94^{239} , in a volume of about 18 cc, together with a few inorganic (such as AgNO_3 and K_2SO_4) and other contaminants. They began by removing the 94 as the insoluble fluoride by co-precipitation with a milligram of La^{+3} . This precipitate was dissolved in a volume of 1 ml with the help of H_2SO_4 , oxidized with $\text{S}_2\text{O}_8^{-2} + \text{Ag}^{+2}$ in the presence of 1 M HNO_3 , and the La^{+3} precipitated as the fluoride by the addition of HF. After removal of the precipitate, two drops of 30% hydrogen peroxide were added to reduce the 94 (no visible precipitate appeared), 100 micrograms of La^{+3} were added as carrier, and the lanthanum fluoride precipitate incorporating the reduced 94 was removed by centrifugation. This precipitate was dissolved in 250 cubic millimeters of H_2O with the help of H_2SO_4 , and the solution again oxidized in the same manner. The La^{+3} was precipitated as the fluoride, and after its removal the 94 was reduced by fuming with H_2SO_4 in a platinum microcrucible and precipitated as the hydroxide in carrier-free form by the addition of five drops of concentrated NH_4OH . The hydroxide was packed by centrifugation in a microcone, dissolved in concentrated HNO_3

solution to which KIO_3 was added to precipitate in carrier-free form plutonous iodate. This appeared as a white bulky crystalline material. After washing with HNO_3 and KIO_3 solution, the iodate was transformed into a pale yellowish green flocculent 94 hydroxide by the addition of concentrated NH_4OH . Measurements on the alpha activity in the supernatant solutions indicated a solubility of about 0.020 grams 94 per liter for the plutonous iodate [whose formula is presumably $\text{Pu}(\text{IO}_3)_4$] and about 0.004 grams 94 per liter for the plutonous hydroxide [whose formula is presumably $\text{Pu}(\text{OH})_4 \cdot \text{XH}_2\text{O}$], using the name "plutonium" for element 94 as suggested by Wahl and me in our Report A-135 ("The Chemical Properties of Elements 94 and 94") issued last March. The pure hydroxide was dissolved in concentrated HNO_3 and upon evaporation to dryness, the lemon-yellow crystalline plutonous nitrate [presumably of formula $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$] appeared. This was dissolved in a small volume of water resulting in a solution of pale yellow-green color. A portion of this solution was delivered onto a platinum weighing boat which had been weighed on our Salvioni balance. The sample was dried and ignited to form the plutonium oxide and the boat was again weighed. By subtraction the weight of the oxide was found to be 2.77 micrograms.

This is the first weighing of pure plutonium, in fact the first weighing of any synthetic element, making

this a historic day. I intend to preserve this sample, for posterity, even though it means removing a precious quantity of plutonium from our experimental program.

[This sample was later photographed by Covey (see Fig. 4). It has been preserved and is now on display in the Lawrence Hall of Science on the Berkeley campus of the University of California.] I am glad that I was present to keep in touch with today's dramatic events. The alpha activity of the sample was roughly determined to be about 263,000 disintegrations per minute, which corresponds to a disintegration rate of about 110,000 alpha particle disintegrations per minute per microgram of plutonium element, assuming the formula of the oxide to be Pu_2O_5 and the molecular weight of plutonium to be 239. (We assume the counting efficiency of our "inside" alpha-particle counter, used to measure the alpha-particle emission rate of an aliquot sample, is 45%.)

We have now seen pure compounds of 94 (plutonium) and weighed a compound of plutonium, results which should give great impetus to the Met Lab's program of producing and separating gram and kilogram quantities of this treasured element.

War front reports are all depressing today. The Nazis claim they have driven to the edge of Stalingrad. At the same time the Japanese have broken through a mountain range in Guinea and are only 44 miles from Port Moresby, keystone of New Guinea defenses.

The descriptions of the first isolation and first weighing of plutonium that appeared in Metallurgical Laboratory Reports at that time have been reproduced in a Benchmark Book of reprints (Seaborg, 1978).

The work of Cunningham and Werner continued the next day:
Friday, September 11, 1942

Today Cunningham and Werner worked on the remaining plutonous nitrate solution of yesterday. They converted the plutonium to the hydroxide by the addition of NH_4OH , dissolved this in HNO_3 and precipitated the iodate by the addition of saturated KIO_3 solution. After washing, this precipitate was converted to the hydroxide by the addition of concentrated ammonium hydroxide, washed, dissolved in acid and then reprecipitated as the hydroxide. As Cunningham and Werner's notebook states at this time, this hydroxide precipitation was made "for the purpose of displaying the pure material to certain interested persons. After this material was returned..." You can imagine how interested we were in showing off and photographing this pure compound. After this digression for the benefit of display purposes, the hydroxide was converted to the nitrate by solution in nitric acid and evaporation to dryness. An aqueous solution of this was placed on a weighed platinum boat, evaporated and ignited and found to weigh 4.45 micrograms, corresponding to 4.02 micrograms of plutonium on the more reasonable assumption

that the formula of the oxide is PuO_2 . The oxide dissolved fairly readily in hot concentrated H_2SO_4 , presumably due to the formation of the stable soluble complex of Pu^{+4} with sulfate ion for which we have previous evidence. An alpha particle count on an aliquot of this indicates that the total alpha activity in the sample is 672,000 alpha disintegrations per minute. This corresponds to a specific activity of 167,000 alpha disintegrations per minute per microgram, which leads to a half-life value of $20,000 \pm 2,000$ years for 94^{239} .

Other Investigations

The group in Berkeley with W. M. Latimer also contributed to this ultramicrochemical program of investigation. During the summer of 1942, A. C. Wahl was also processing cyclotron-irradiated uranium in order to isolate pure plutonium. He isolated 200 micrograms of chemically pure plutonium in 92 per cent yield from 45 kilograms of uranium that had been irradiated for two months with neutrons from the Berkeley 60-inch cyclotron. He employed lanthanum fluoride precipitations from reduced and oxidized solutions and measured yields and decontamination factors at every step, collecting data which proved very valuable in evaluation of this separations process, then the only practical method for isolation of plutonium. The chemical procedure was started in July, but progress was slow because of the care exercised in evaluation of the separations process, and a pure compound of plutonium (IV)

hydroxide, was not isolated until September 29, 1942. Wahl was very pleased to show the 0.2 milligram plutonium sample, easily visible to the naked eye, to E. O. Lawrence, whose cyclotron had produced the plutonium. This plutonium was used in an ultramicrochemical program of investigation at Berkeley. Among other accomplishments, the Berkeley chemists were able to establish in 1943 that the oxidation number of the highest state is VI (Connick and co-workers, 1949).

Some continuing ultramicrochemical investigations of Cunningham and Werner are described in my journal.

Monday, September 28, 1942

Upon returning to Jones Laboratory this morning, I found that my group has been extremely active all week during my absence.

Cunningham, Werner, and Cefola have spent the last two weeks doing experiments and recovering the 94 from the various fractions and residues following their experiments using 94 from Perlman's, Kohman's, and Jaffey's batches. Cunningham and Werner have prepared a "stock solution" of pure 94 nitrate containing about 2γ (micrograms) of 94 per λ (cubic millimeter) of solution. This they plan to use to test the solubilities of a number of 94 compounds to give information that might be useful in developing a procedure for the separation of 94 from uranium and fission products in neutron-bombarded uranium from a pile. They have perfected methods for the determination of solubility of 94 compounds.

In their experiments a small amount of 94 nitrate (containing approximately 0.1 γ 94) is placed in 2 λ of solution, the appropriate precipitating agent added, the mixture centrifuged, the supernatant liquid removed and replaced by about 5 λ of the medium in which the solubility of the compound is to be measured. The two phases are mixed by vigorous stirring, allowed to stand overnight or longer at room temperature ($25^{\circ}\text{C} \pm 5^{\circ}\text{C}$). Then a measured volume of the supernatant is withdrawn and its alpha activity determined. Solubilities of 94 (plutonium) are calculated in terms of the concentration of the element, assuming the specific activity to be 167,000 alpha disintegrations per microgram of plutonium per minute (half-life of 20,000 years).

On Saturday, upon measuring the supernatants of the various precipitations performed the day before, Cunningham and Werner found the following solubilities:

<u>Precipitant</u>	<u>Compound</u>	<u>Medium</u>	<u>Solubility (mg Pu/liter)</u>
KIO ₃	plutinous iodate	sat'd KIO ₃ soln	2.1
"	" "	1/2-sat'd KIO ₃	1.8
"	" "	sat'd KIO ₃	4.8
"	" "	3 M HNO ₃	
"	" "	sat'd KIO ₃	6.2
"	" "	6 M HNO ₃	
HF	plutinous fluoride	H ₂ O	10.8
"	" "	3 M HF	12.3

<u>Precipitant</u>	<u>Compound</u>	<u>Medium</u>	<u>Solubility (mg Pu/liter)</u>
HF	plutonous fluoride	6 M HF	44.8
NH ₄ OH	plutonous hydroxide	H ₂ O	1.8
"	" "	conc. NH ₄ OH	0.24

Also on Saturday Cunningham and Werner received Goldschmidt's one-fourth portion of 94^{239} (batch No. 4) from the large St. Louis neutron bombardment of uranium. This consists of about 8×10^6 alpha-particle disintegrations per minute, corresponding to about 70 micrograms of 94^{239} in a volume of 25 cc. To this they added about 3×10^6 alpha-particle disintegrations per minute that they have recovered from the residues of Kohman's and Jaffey's portions during the last couple of weeks.

An important experiment was the establishment of the +4 oxidation state of plutonium:

Tuesday, October 13, 1942

Cunningham and Werner prepared a sample of plutonium iodate from a small portion of their stock plutonium nitrate solution by the addition of excess HIO₃ in 4 M HNO₃. The precipitate was removed by centrifugation, washed with H₂O, transferred to a platinum weighing boat, dried for four hours at 100°C, then weighed with the Salvioni balance. The precipitate was then dissolved and the dried platinum boat was weighed again giving a weight of 1.70 micrograms for the plutonium iodate. The alpha-particle activity of the dissolved iodate was determined and found to be

73,000 alpha disintegrations per minute. Using a specific activity for plutonium of 165,000 alpha disintegrations per minute per microgram, this corresponds to 0.44 micrograms of plutonium element. From this we can calculate the mole ratio of iodate to plutonium to be 3.89, pointing strongly to a valence charge of +4 for the plutonium in plutonous iodate. This is the first instance in which the formula for a plutonium compound has been established. The formula, $\text{Pu}(\text{IO}_3)_4$, agrees with our expectations.

Move to New Chemistry Building

By October 1942, my research group had grown to about 25 members, completely saturating the laboratory space that had been allotted to us on the fourth floor of the George Herbert Jones Laboratory (Fig. 5). In anticipation of this, construction of a new building was nearing completion to house my group and other chemists on the Plutonium Project, at a site on Ingleside Avenue (between 56th St. and 57th St.) at the edge of the University of Chicago campus (Fig. 6). We moved into this building --the New Chemistry Building--during December and by the following April (1943) our group (now called Section C-I) had doubled in number to about 50 people (Fig. 7).

The Bismuth Phosphate Process

Stanley G. Thompson joined my group on October 1, 1942 and it fell to his lot to discover the process that was chosen for use at Clinton Laboratories (in Tennessee) and the Hanford Engineer Works (in the state of Washington) for the separation

of plutonium from uranium and the immense intensity of radioactive fission products with which it was produced in the nuclear chain reactors. Again I turn to my journal to tell the story:

Saturday, December 19, 1942

Today Thompson tested the use of bismuth phosphate as a carrier for 94 in its reduced state with rather encouraging results. Upon precipitating relatively high concentrations of bismuth (15-25 mg per 10 cc) as bismuth phosphate from 20% UNH solution, he finds the 94 to be carried to the extent of more than 85%. The bismuth phosphate precipitates are slow in forming and require digestion at temperatures of the order of 75°C. He finds that the bismuth phosphate precipitate is very dense and crystalline, which are desirable properties, and dissolves readily in HCl.

In view of Thompson's results on the carrying of Pu^{+4} by bismuth phosphate, Cunningham and Werner made an immediate test today to see whether it is carried at a ratio of $\text{Bi}^{+3}:\text{Pu}^{+4}$ of about 100:1. Their results indicate that under conditions similar to those of Thompson's experiment, the Pu^{+4} is carried to the extent of 98%. This was fast work and illustrates the pace at which our group is now working. They also made a test of the carrying of Pu^{+4} by hafnium phosphate at a ratio of Hf:Pu of 100:1 and they find that about 90% of the Pu is carried.

The reason for the ultramicrochemical test was to establish whether the bismuth phosphate would carry the plutonium at the concentrations that would exist at the Hanford extraction plant. This test was necessary because it did not seem logical that tripositive bismuth should be so efficient in carrying tetrapositive plutonium. In subsequent months there was much skepticism on this point and the ultramicrochemists were forced to make repeated tests to prove this point. Thompson soon showed that Pu(VI) was not carried by bismuth phosphate, thus establishing that an oxidation-reduction cycle would be feasible. All the various parts of the bismuth-phosphate oxidation-reduction procedure, bulk reduction via cross-over to a rare earth fluoride oxidation-reduction step and final isolation by precipitation of plutonium (IV) peroxide were tested at the Hanford concentrations of plutonium in careful and crucial experiments performed by Cunningham, Werner, Perlman, Daniel R. Miller, and others. Without the possibility of these tests early in 1943, I believe that this process, which went into production at Hanford in the state of Washington, and which performed exceedingly well, would not have been chosen. Several alternative processes, including solvent extraction, volatility, adsorption and other precipitation methods were also under investigation, but these either were beset with problems or were not sufficiently developed and the choice of one of them could very well have delayed the date of obtaining the final product plutonium in the required quantities.

Discovery of Other Fundamental Chemical Properties

The first definite production of plutonium metal was made in November, 1943 by Baumbach and coworkers (1958). Approximately 35 micrograms of PuF_4 in a small thoria crucible in a high vacuum was reacted with barium metal at 1400°C to yield plutonium metal. The metal was found to have a silvery lustre, a density of about 16 grams per cubic centimeter and it rapidly absorbed hydrogen at about 210°C to form a black powder subsequently identified as PuH_3 (a proof that metal had been produced).

The successful operation of the reactor and plutonium extraction plant at Oak Ridge, Tennessee led to the availability of first milligram, and then gram, amounts of plutonium/starting in 1944. The availability of milligram amounts of plutonium led to the immediate discovery of the III oxidation state. As mentioned above, early tracer work at the University of California in 1941 had established the existence of a lower oxidation state (IV and/or III state) and a higher state (VI and/or higher state), and the ultramicrochemical work late in 1942 and in 1943 had defined the existence of the IV and VI states. The III oxidation state was discovered early in 1944 by Connick and coworkers (1949), who actually worked with about 0.25 milligram of cyclotron-produced plutonium, at the University of California, Berkeley, and, essentially simultaneously, by Hindman and coworkers (1949) at the Metallurgical Laboratory and Mastick and Wahl (1944) at the Los Alamos Laboratory; the latter two groups utilized the milligram amounts of plutonium made available at the time through the operation of the reactor and

chemical separation plant at the Clinton Laboratories in Tennessee. The existence of the V oxidation state was established in the summer of 1944, through the use of plutonium obtained from the Clinton Laboratories, by Connick and coworkers (1949), at the University of California, Berkeley.

Although a number of solid compounds of plutonium were synthesized by ultramicrochemical techniques during our first year and a half at the Metallurgical Laboratory, it was not until November, 1943 that a positive identification of a crystal structure was made. W. H. Zachariasen joined the project in the fall of 1943 and very soon began to make definitive identifications of compounds on the microgram scale using the x-ray diffraction technique. The first positive result was obtained on plutonium dioxide:

Monday, November 8, 1943

In the course of their attempts to produce powdered plutonium metal suitable for study by the x-ray diffraction method, Kirk and Baumbach submitted a sample that turned out to be plutonium dioxide weighing 10 micrograms which they gave to Zachariasen last Wednesday; he succeeded in obtaining a satisfactory x-ray diffraction pattern, enabling him to determine its crystal structure. This is a tremendous accomplishment! This probably means that it is possible, even on a microgram scale, to obtain the structure of numerous plutonium compounds. This would be a tremendous boost to our program. Consider the following results. The oxide has the fluorite structure. There are

four molecules in the unit cube which has an edge equal to $5.370 \pm 0.005 \text{ \AA}$. The density of the oxide is 11.54 gm/cm^3 . For comparison, the edge of the unit cube of thorium oxide and uranium oxide is 5.58 and 5.47 \AA , respectively. All of this information was obtained with 10 micrograms!

The ingenuity and experimental skill displayed by the microchemists in devising methods for conducting dry-chemical reactions in tiny, thin-walled capillary tubes, and the astonishing ability of Zachariasen in securing and interpreting x-ray diffraction patterns on products so prepared, led to the identification of a large number of plutonium compounds. Although the first such work was performed with the small (microgram) quantities of cyclotron-produced plutonium, more progress was made when the larger amounts became available from the operation of the pilot production plant at Clinton Laboratories in Tennessee (first milligram and then gram amounts) early in 1944, and when the still larger amounts became available from the production plant at the Hanford Engineer Works in the state of Washington early in 1945. During this period, all of the binary halides as well as the oxides and oxyhalides and several other compounds of plutonium were synthesized and identified. It was also possible to obtain basic thermodynamic data on a number of these compounds by direct thermochemical methods or by observations of the temperature coefficients of equilibrium constants or, as rough

estimates, by noting the presence or absence of reactions under chosen experimental conditions to establish lower or upper limits of stability.

A good deal was learned about plutonium metal, including the determination of ^{its} density by both capillary displacement and x-ray diffraction methods, its melting point and vapor pressure.

Much was also learned at the Metallurgical Laboratory about the solution chemistry of plutonium during these first few years of investigation. This included elucidation of the ionic species present in aqueous solutions of different acids and determination of the nature of various complex ions. The group at Berkeley made notable contributions to measuring the oxidation potentials relating the various oxidation states and toward understanding the kinetics of reactions involving these states. The group at Los Alamos also added much to this knowledge, especially about methods for production of the metallic state and the properties of the metal.

Thus, a large amount of information about the chemical properties of plutonium, working with macroscopic or weighable amounts, was obtained during those first few years, i.e., 1942 to 1945. Until the fall of 1943, cyclotron bombardments were the sole source of plutonium and a total of about 2000 micrograms, or 2 milligrams, were prepared. When the larger amounts became available from Clinton Laboratories early in 1944 and still larger amounts from the Hanford Engineer Works early in 1945, the amounts available to the chemists were still relatively

small and the investigations continued on the microchemical scale.

Subsequent Investigations

Investigations of the chemical properties of plutonium have continued in many laboratories throughout the world as it has become available. This has led to the situation where the chemistry of this relative newcomer is as well understood as is that of most of the well-studied elements. The four oxidation states of plutonium--III, IV, V, and VI--lead to a chemistry which is as complex as that of any other element. It is unique among the elements in that these four oxidation states can all exist simultaneously in aqueous solution at appreciable concentration. As a metal, also, its properties are unique. Metallic plutonium has six allotropic forms, in the temperature range from room temperature to its melting point (640°C), and some of these have properties not found in any other known metal.

This account of the beginnings and early days of the forty years of plutonium chemistry should serve as a background for the following papers which illuminate many of the accomplishments of the intervening years and emphasize the high level of the present status of information on the chemical properties of this remarkable synthetic element.

Acknowledgements

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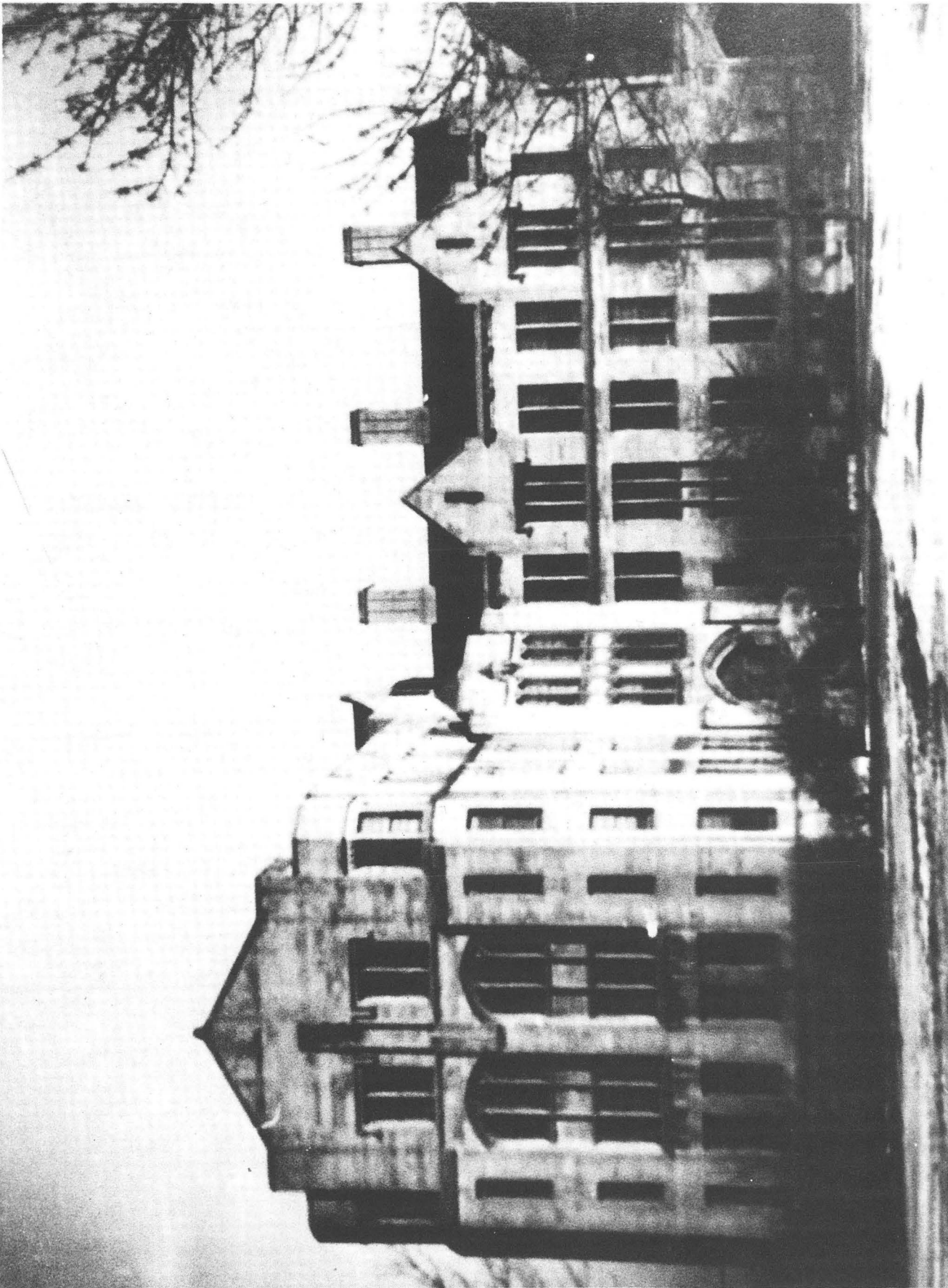
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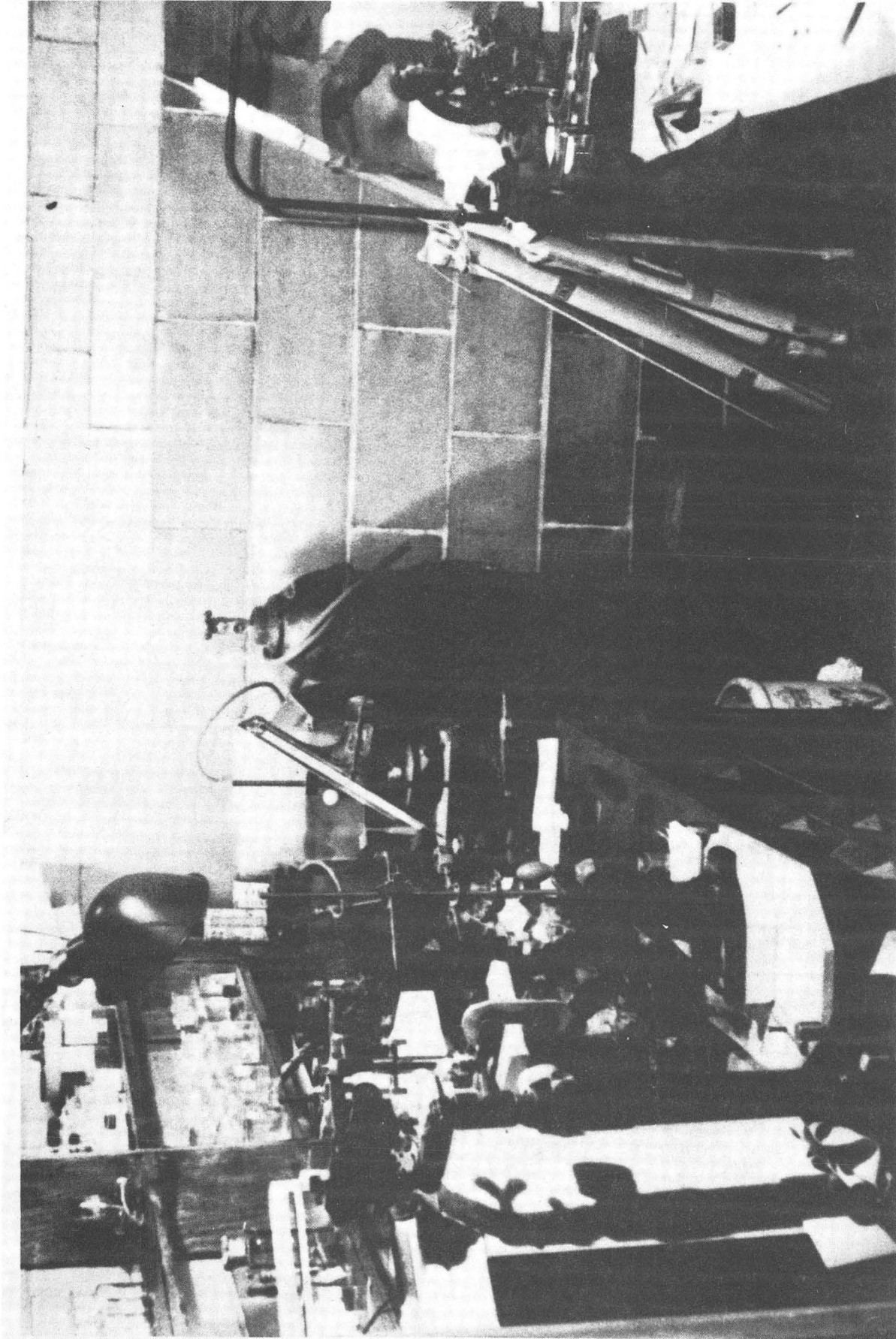
Captions

- Fig. 1. George Herbert Jones Laboratory. Our laboratory space on top (fourth floor) of wing at left. Roof top work area at right end of right wing. (XBB 768-7453)
- Fig. 2. Room 405, Jones Laboratory, August 20, 1942. (XBB 768-7455)
- Fig. 3. L. B. Werner and B. B. Cunningham, Room 405, Jones Laboratory, August 20, 1942. (XBB 768-7456)
- Fig. 4. Plutonium oxide (2.77 micrograms) weighed on September 10, 1942. It is shown on a platinum weighing boat magnified approximately 40-fold. The plutonium oxide appears as a crusty deposit (indicated by the arrow) near the end of the platinum weighing boat, which is held with forceps that grip a small handle (upper part of photograph). (CHEM 1146)
- Fig. 5. Space occupied by individual members of our group, early October 1942 on fourth floor of Jones Laboratory. (XBL 768-3256)
- Fig. 6. New Chemistry Building under construction, October 1942. Facing east from Ingleside Avenue. Main entrance in view beyond top of car. (XBB 768-7460)
- Fig. 7. Room assignments of members of Section C-I, late April 1943, in New Chemistry Building. (XBL 768-3255)



XBB 768-7453

Figure 1



XBB 768-7455

Figure 2

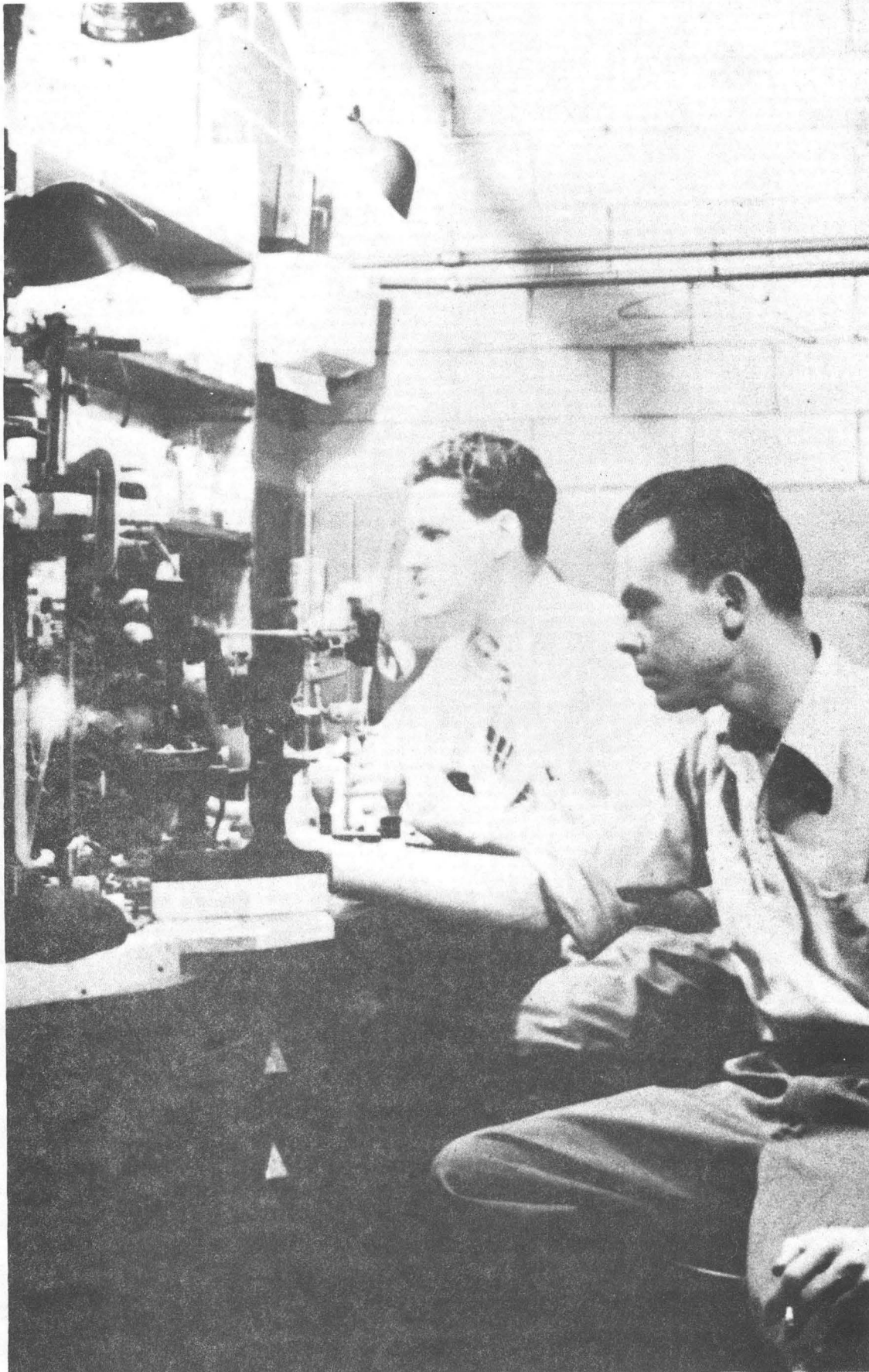


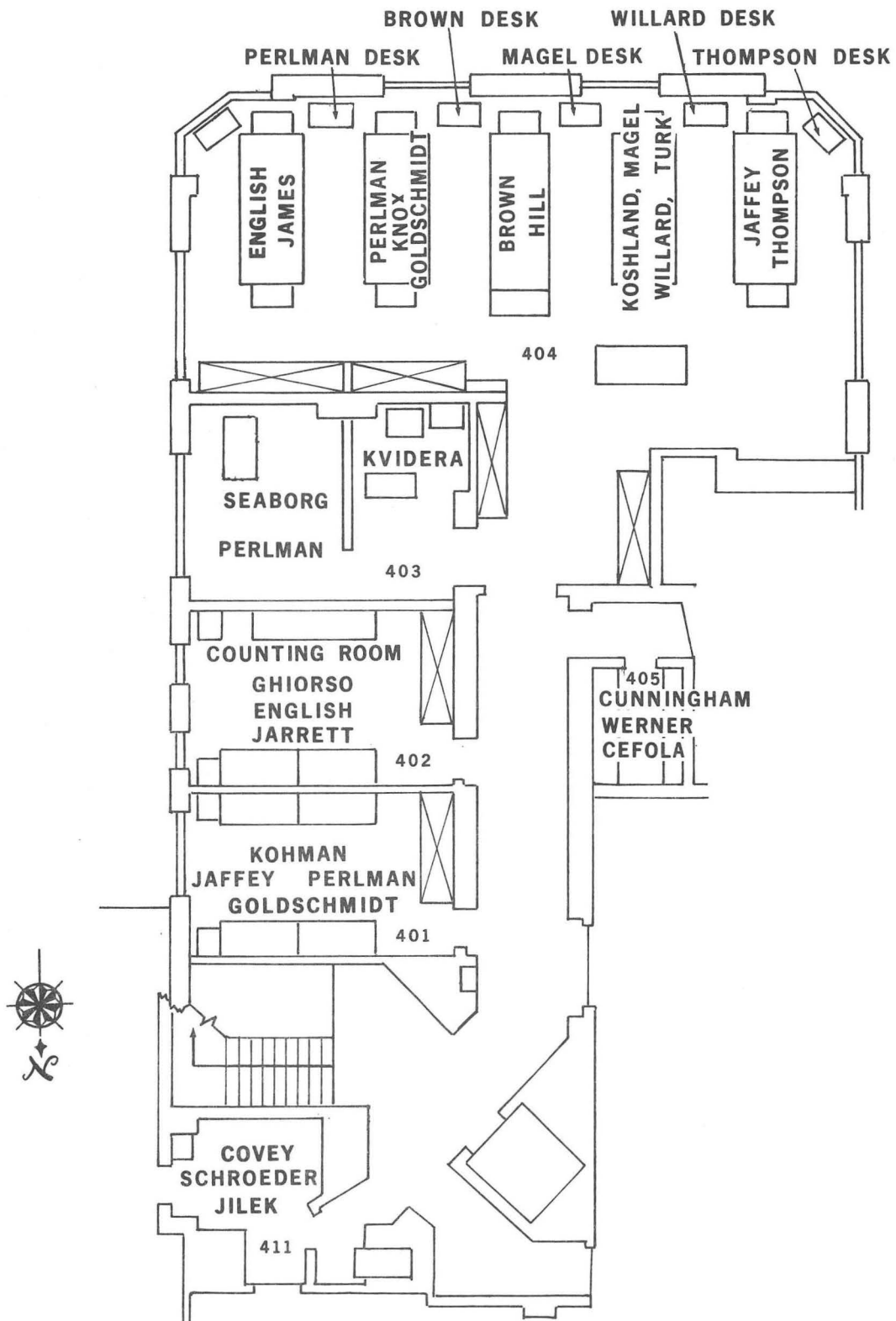
Figure 3

XBB 768-7456



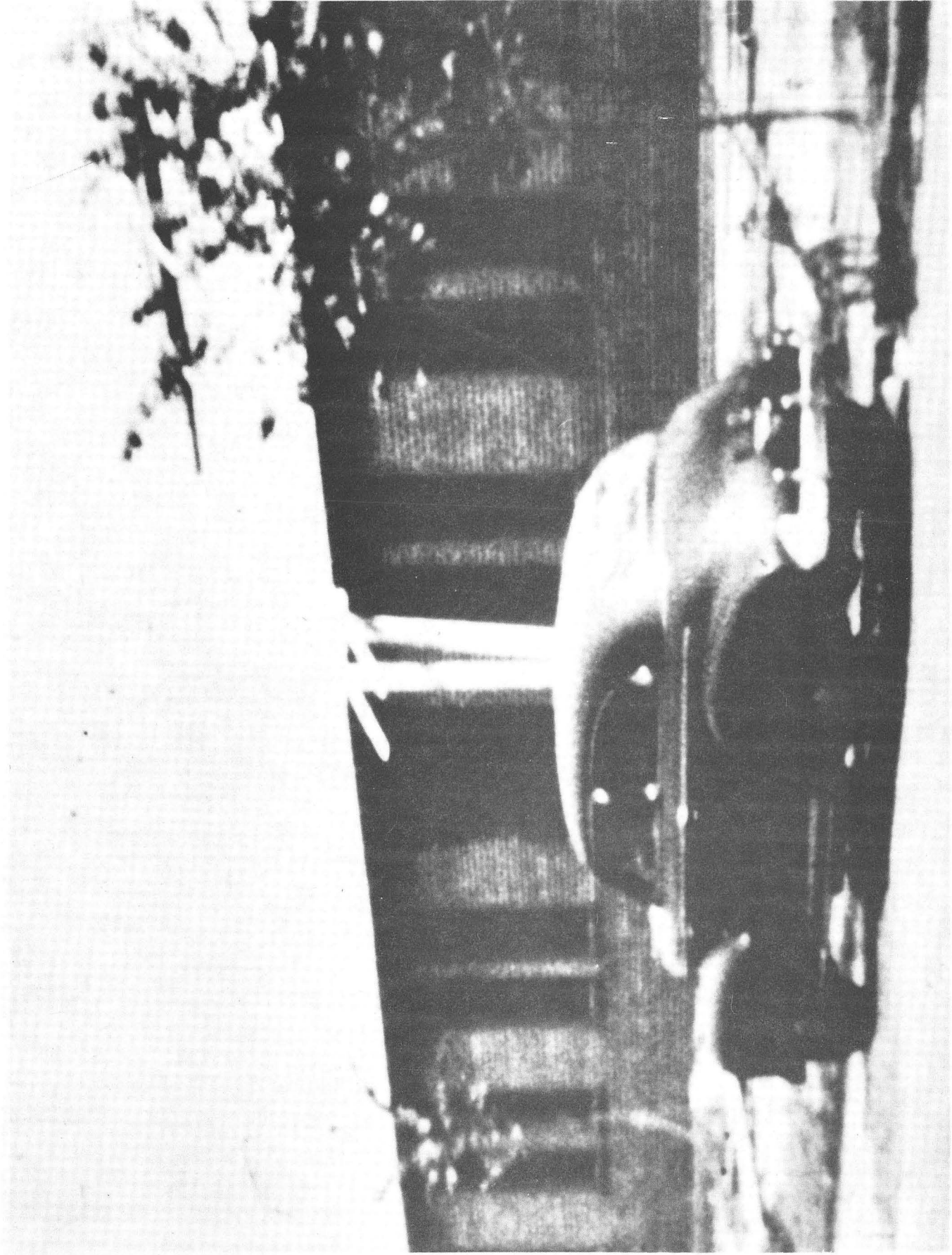
CHEM 1146

Figure 4



XBL 768 - 3256

Figure 5



XBB 768-7460

Figure 6

5 KOHMAN JAMES KOSHLAND	4 THOMPSON DAVIDSON COOPER DREHER MILLER	3 OSTAPOWICZ	2 STOUGHTON KATZIN BOHLMANN BOND	BROWN HILL SCHULZE JAFFEY	1 MAGEL DALLAS
6 PERLMAN ORLEMANN KATZ KNOX	7 JARRETT SCOTT	8 CUNNINGHAM	9 WERNER CEFOLA SMITH PATTON N BAUMBACH	10 WILLARD TURK BEATON FRIES LA CHAPELLE SHEFT	11 COVEY SUMMERS PAULSEN FULAN YOUNG
	14 THARPE E. SMITH MOORE	13 KIRK H BAUMBACH ROSENFELS			
	15 SEABORG PERLMAN				
	16 ENGLISH GHIORSO J. CRAWFORD				

Figure 7

XBL 768 - 3255

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