

Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

Title

University of California Radiation Laboratory Progress Report for November, 1947

Permalink

<https://escholarship.org/uc/item/9z3722d1>

Author

Perlman, I.

Publication Date

2010-01-19

Peer reviewed

DECLASSIFIED

UCRL 15

~~SECRET~~

UNIVERSITY OF
CALIFORNIA

C. 2

Radiation Laboratory

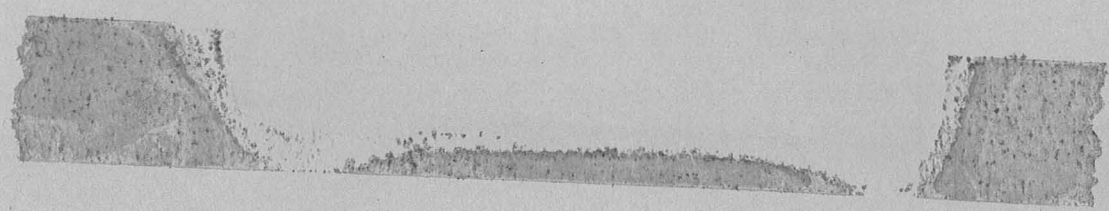
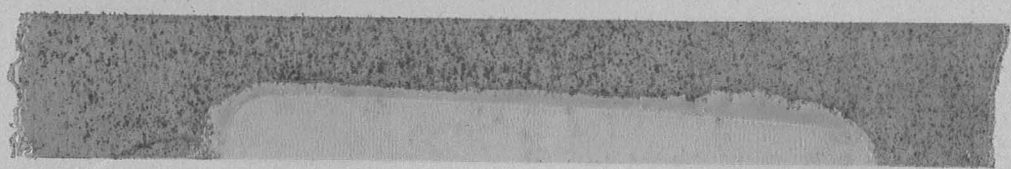
TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

UCRL-15
C. 2

1947



INDEX NO. UCRL-15
This Document Contains 14 Pgs,
and 0 Plates of Figures.
This is Copy 59 of 65, Series A

DECLASSIFIED

DO NOT REMOVE THIS PAGE

Issued to: ISLON

~~THIS IS A CLASSIFIED DOCUMENT~~

~~(Classification to be stamped here)~~

1. This document contains information affecting the National Defense of the United States within the meaning of the Espionage Act, U. S. C. 50; 31 and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.
2. Before this document can be given to a person to read, his name must be on the Reading List of those authorized to read material on this subject, or permission must be obtained from the Information Division or the Executive Office.
3. A SECRET or CONFIDENTIAL document is to be kept only in a guarded area. When stored, it must be kept in a locked safe or in a locked filing case with a tumbler lock.
4. A SECRET or CONFIDENTIAL document is not to be copied or otherwise duplicated without permission of the originating office. Extensive notes on the contents of a secret report may be taken only in a bound notebook with numbered pages, having the designation SECRET. This must be safeguarded in the same way as a Secret Report (See 1, 2 and 3). Other notes must be avoided, but if made must be done in a form meaningless to anyone but the writer and later destroyed.
5. The person or office to whom a SECRET or CONFIDENTIAL document is issued is accountable for the document at all times. A system of accountability by signed receipts or a signed record book must always be used. Permission for transmission to another office than that of the assignee must be obtained through the Information Division and recorded there.
6. After a document passes the stage of usefulness to its possessor, it should be returned to the Information Division, whereupon the individual will be relieved of the responsibility for its safe-keeping.
7. Initial and date the pages of this document which describe any work that you have witnessed, adding any pertinent information, such as references to original work records. This document, properly signed, dated and annotated, is important in patent preparation.
8. Each person who reads this document must sign this cover sheet below. Please sign and date the cover sheet after reading the report. Also state by Yes or No whether or not notes have been taken. See paragraph 4 above.

Route to	Read By	Notes?	Date	Route to	Read by	Notes?	Date
			3/14/51				

~~CONFIDENTIAL~~
~~CONFIDENTIAL~~
~~CONFIDENTIAL~~

<u>Distribution of UCRL-15/A</u>	<u>No. of Copies</u>
Argonne National Laboratory	10
Atomic Energy Commission, Washington	3
Brookhaven National Laboratory	8
Clinton Laboratories	8
General Electric Company	4
Hanford Engineer Works	2
Iowa State College	1
Los Alamos	3
Madison Square Area	1
Patent Advisor	1
Research Division (for NEPA), Oak Ridge	1
Research Division, Oak Ridge	15
University of California, Radiation Laboratory	
Information Division	2
Chemistry Department	
(G.T. Seaborg)	1
W. Latimer	1
M. Calvin	1
Patent Department	1
University of Rochester	2
TOTAL	<u>65</u>

Special Review of Declassified Reports

Authorized by USDOE JK Bratton

Unclassified TWX P182205Z May 79

REPORT PROPERLY DECLASSIFIED

_____ 8-15-79
 Classifier Date

_____ 8-20-79
 Date

Radiation Laboratory
 Information Division
 University of California
 Berkeley, California

DECLASSIFIED

~~SECRET~~

15

This document contains 14 pages and 0 figures.

Copy 57 of 65, Series A.

UNIVERSITY OF CALIFORNIA RADIATION LABORATORY

PROGRESS REPORT FOR NOVEMBER, 1947. CHEMISTRY SECTION

PART A. REPORTED BY I. PERLMAN

Contract No. W-7405-eng-48

CLASSIFICATION CANCELLED
DECLASSIFICATION
RENT ID 1112
- 3-12-56
DATE

SIGNATURE OF THE
PERSON MAKING THE
CHANGE

Chemistry and Structure of the Actinide Elements

Preparation of NpCl₄

NpCl₄ has been prepared by reacting NpO₂ with AlCl₃. The AlCl₃ was sublimed into the NpO₂ in a dry argon atmosphere. The furnace was heated to 250° C for seven hours, after which the AlCl₃ was sublimed and pumped off. The residue was heated to about 500° C and a yellow sublimate was collected which proved to be NpCl₄ by indexing its x-ray diffraction pattern against the lattice structure reported by Zachariasen.

Crystal Structure of AmO₂

The dioxides of the heavy elements uranium, neptunium, plutonium and americium have a fluorite structure and the lattice constants would be expected to lie on a smooth curve. Zachariasen has determined these lattice constants and found them to do so although an irregularity showed up with americium. This irregularity was attributed to lanthanum contamination in the AmO₂ and when corrected for this the irregularity was largely overcome.

A sample of AmO₂ has been prepared with pure americium and its lattice constant determined to be a = 5.376 ± 0.001. This value is within the range of the experimental values that Zachariasen obtained with his "impure" AmO₂ and is significantly different from the corrected value and from the extrapolation of

~~SECRET~~

~~CONFIDENTIAL~~

the U-Np-Pu curve. This would suggest that americium behaves in a manner similar to praseodymium in which mixed oxides are obtained corresponding to the formula Pr_6O_{11} .

Preparation of Actinide and Lanthanide Metals

The method for preparation of heavy metals by reducing the fluorides with barium has proved quite successful in the cases of uranium, neptunium, and plutonium but only a couple out of many tries resulted in metal when americium fluoride was reduced in a similar manner. It has recently been found here that of the rare earths europium metal also cannot readily be produced in this fashion, confirming similar difficulties on a larger scale reported by F. H. Spedding. Using the same method (in which americium and europium could not be prepared) on neodymium, it was found that metal preparation occurred readily. Similarly, plutonium was again checked and found to give good metal preparations. It would appear therefore that by the barium reduction method the so-called "divalent metals" like europium among the rare earths and americium among the actinide elements, behave similarly. This is another piece of evidence for considering europium and americium homologues.

Nuclear Properties of the Heavy Elements

Possible Alpha-Branching of Np^{235}

The nuclei of odd atomic number are characterized by a single-- or at most two--beta-stable isotopes, and in searching for regularities in alpha-decay properties it is therefore most difficult to obtain data from these elements. However, since all isotopes in the region of heavy elements should be unstable with respect to alpha-emission it may, in some cases, be possible to see the alpha-emission of beta-unstable isotopes if the branching is

~~CONFIDENTIAL~~

appreciable. Recently the orbital electron capturing isotope Np^{235} with 400-days' half-life has been prepared by the (d,2n) reaction on U^{235} . In the neptunium and plutonium fraction from this bombardment there was a great deal of alpha-activity from Pu^{236} arising from the beta-decay of 22-hour Np^{236} produced by the (d,n) reaction. When the plutonium was carefully separated from the neptunium a small amount of alpha-activity persisted which had a range corresponding to about 5.0 Mev energy. It will be necessary to ascertain whether or not this activity decays with the same half-life as the Np^{235} x-rays before it can be definitely assigned to alpha-branching of this isotope.

Nuclear Reactions with High Energy Particles

Spallation Reactions on Tantalum with 200-Mev Deuterons

The region below tantalum is being investigated in order to determine the products of spallation reactions and therefore the types of reactions which occur in this region. This includes the region of the rare earth elements and therefore special chemical methods are necessary. The methods of operation involve the separation of the rare earths as a group from tungsten, tantalum, hafnium and rhenium, after which the rare earths are separated by an adsorption column using nalcite resin and citrate solution for elution. The column separation of the rare earths is also being used in the identification of the fission products of heavy elements like americium where it is now apparent that fission activities appear well up into the rare earth region.

The rare earth separation was tried out using inactive macroscopic amounts of the rare earths and analyzing spectroscopically the eluate from the column at short intervals. The method which

~~SECRET~~

proved to be successful used a 50 cm. column 0.4 cm. in diameter, the citrate solution at pH 3.03 and a flow rate of 1.5 ml./cm.²/min. 0.5 mg. of each rare earth was used in the starting mixture. The ytterbium, thulium, erbium, holmium and dysprosium fractions had no detectable impurities; the lutecium contained 0.2% ytterbium and the europium and gadolinium fractions overlapped considerably. Yttrium was also present and was spread out over the europium, gadolinium and part of the samarium peak.

All of the activities from the reaction of tantalum with 200-Mev deuterons have not yet been separated and identified but it is already apparent that the highest yields appear in the immediate neighborhood of the target element and then there is a gradual decrease in yields through about five atomic numbers (12 mass units) after which there is a sharp drop in yield for isotopes of lower elements. This same characteristic distribution has showed up in bombardments of antimony, arsenic and copper and suggests that the most probable reactions are those with single nucleons of the deuteron, which type of reaction cuts off with the ejection of some 12 particles. The much lower yields obtained for reactions which produce nuclei farther away would then be caused by the 200-Mev deuteron itself forming a compound nucleus rather than only one of its two nucleons doing so.

meb
12-5-47

~~SECRET~~

PART B. ASTATINE CHEMISTRY

REPORTED BY R.F. LEININGER

Migration experiments described last month were completed for astatine. Some experimental errors were found and the following final results obtained. In the solutions listed below the astatine migrated as a negative ion. In all cases, the astatine was first dissolved in concentrated nitric acid.

Diluting Agent	Molarity	pH	Oxidizing Agent	Reducing Agent
Water	5M			
Water	1M			
Water	.1M			
Phosphate buffer		5		
Phosphate buffer		8		
Phosphate buffer		11		
NaOH	0.1M			
NaOH	0.1M			Na ₂ SO ₃
Water	0.1M			SO ₂
NaOH	0.1M		NaClO	
Water	0.1M		K ₂ S ₂ O ₈	
Water	5.0M		K ₂ S ₂ O ₈	

No migration as a positive ion was observed and no good evidence was found for the presence of a weak astatine acid.

The distillation of astatine dissolved in CCl₄ was done. The results are summarized below. 10 ml of CCl₄ solution were used and 8 3/4 ml of distillate were collected in 1 ml amounts.

Aliquot	Distillation of Astatine in CCl ₄ Solution	
	Percent of Total	Percent of Total
1st ml	1.1	6th ml .79
2nd ml	.78	7th ml 1.00
3rd ml	.73	8th ml 2.01
4th ml	.61	3/4 ml 7.80
5th ml	.61	Still pot residue 64.0

The over-all material balance was 78.4 percent. Considerable activity was left in the still pot. Since a simple distillation apparatus was used the initial activity appearing in the distillate could easily be due to entrainment. Since the CCl₄

solution was added from the top of the apparatus the initial decrease is probably due to washing down of the distillation column walls into the condenser.

Experiments on the solvent extraction of astatine by CCl_4 and benzene are in progress. To date extraction coefficients of ~ 85 and ~ 110 have been obtained between 0.01M HNO_3 solution of astatine and CCl_4 and benzene respectively when the extraction is performed in 0.01 M NaOH, coefficients of 1 or less are found. If, however, the aqueous layer is acidified (0.1M HNO_3) and the layers recombined and reextracted, large coefficients are again obtained. The only possible explanation so far considered is the disproportionation of the astatine in the zero state into a positive and a negative valance state. Since the only ions so far observed are negative, our best guess is At^- and AtO_3^- .

Experiments are in progress using extraction experiments as a tool to determine the approximate oxidation potential of the reaction $\text{At}^- \rightarrow \text{At}^0 + e^-$ or $\text{At}^- \rightarrow \frac{1}{2}\text{At}_2 + e^-$. The best value obtained thus far lies in the range -0.1 to -0.4 volts.

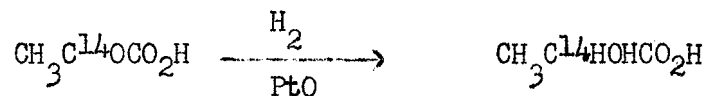
Electrodeposition experiments of astatine or gold from the zero and -1 states were attempted using the method Joliot.⁽¹⁾ No deposition on gold was observed in the potential region +0.2 to -0.6 volts, since one would expect any At^- or At^0 formed on the gold to be soluble in H_2O . The above voltages are for gold with respect to a normal H_2 electrode.

PART C. BIO-ORGANIC CHEMISTRY

REPORTED BY B. TOLBERT

Synthetic and Experimental Chemistry

Lactic acid labeled in the carbon alpha to the carboxyl group has been prepared labeled with C^{14} , and the degradation of this compound studied. Preparation of lactic acid was accomplished by reducing pyruvic acid.



In this reduction 215 mg. of pyruvic acid in 10 ml. of alcohol were treated with hydrogen in the presence of Adam's catalyst (PtO) and ferrous iron at 60-70°C. After the reduction the active lactic acid was about 70 percent. It was not found possible to use acetic acid as a solvent for this reduction. Lactic acid was degraded by a standard method, namely, oxidation with 7 percent chromic acid and 2 N sulfuric acid solution; this oxidation produces carbon dioxide and acetic acid. In this case the acetic acid was labeled in the carboxyl group. The acetic acid was degraded by converting it to barium acetate and pyrolyzing the barium acetate to acetone and carbon dioxide, whereby it was shown that the carboxyl group of the acetic acid was the labeled group; this position corresponds to the alpha position of the lactic acid.

Work has continued on the various phases of the synthetic program among which are the synthesis and degradation of labeled propylene, the synthesis of ethyl alcohol and an improved synthesis of glycine.

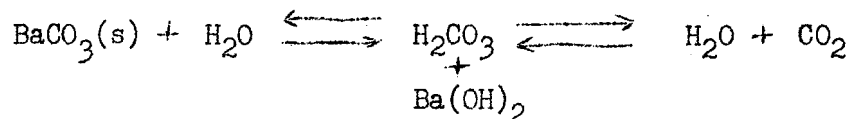
As outlined in last month's progress report, experiments are being done to determine the loss of activity of solid barium carbonate counting samples when exposed to laboratory air. Sets of plates of various weights were placed in controlled and uncontrolled atmospheres and counted at intervals of one week. In the table below are noted the mean total losses at 9 weeks' exposure for several samples. No correlation was noted between the rate of loss and sample thickness in the samples studied, the thinnest of which was 0.53 mg/cm² and the thickest of

which was 3.30 mg/cm².

Table 1

<u>Sample</u>	<u>Condition of Storage</u>	<u>Percent Activity Loss 9 weeks.</u>
U glass	-	1.2
BaCO ₃	This sample was bound to the disk by shellac and should have suffered no loss.	2.0
BaCO ₃	covered Petri dish in an office	2.8
BaCO ₃	synthesis laboratory, no gas burners, rather acid atmosphere	6.0
BaCO ₃	combustion room, several gas burners; acid, wet atmosphere	12.1
BaCO ₃	in an office, uncovered	2.5
BaCO ₃	drying oven in combustion room, high CO ₂ level, alternate wet and dry (mostly dry) atmosphere	3.6
BaCO ₃	in stream of outside air (low CO ₂) saturated with water	3.6
BaCO ₃	in stream of carbon dioxide saturated with water	8.0
BaCO ₃	in sample storage book, (loosely covered, but in drier air than Petri dish samples)	1.0 (5.5 months)
BaCO ₃	dry (CaCl ₂) CO ₂	1.1

These results substantiate predictions one might make on the following exchange scheme.



Thus, both water and carbon dioxide are necessary for exchange. Sensible care in the storage of solid counting samples should prevent serious loss over moderate periods of time.

Biological Chemistry

The distribution of radioactivity following intravenous administration of DL radiotyrosine to mice bearing melanosarcoma has been investigated. After 72 hours, about 30 percent of the administered dose appears in the breath, about 40 percent in the urine and feces, with 30 percent remaining in the body. Radioactivity is found in every tissue of the body. The adrenals, thyroids, intestines, kidneys, liver, plasma, spleen and tumor show the highest specific activities. Erythrocytes are lowest, with bone next. The gross half time for turnover of radioactivity in the body for the period between 12 and 72 hours after administration is 60 hours.

Isolation work has begun on the tumors from mice bearing melanosarcoma to which labeled DL-tyrosine has been administered. It has been found that tyrosine is definitely converted to pigment in the tumor, confirming earlier theories of melanin formation. About half of the total activity of the tumor can be accounted for as melanin and tyrosine.

Work has continued on the administration of dibenzanthracene, tyrosine and other simple radioactive compounds to animals.

Photosynthetic Chemistry.

The work on the role of phosphorus has been studied using radiophosphorus as a primary tool and a report on this has been issued (UCRL-10). It has been shown that phosphorylation, an essential process in metabolism, is not directly involved in photosynthesis. Methods have been developed for studying the rate of exchange of radioactive phosphate ions with the organic cell constituents of the working plant. No difference in rate were found upon illumination of the plant.

As mentioned before, studies are being made on the relationship of prehistory to the dark fixation of algae with respect to the growth and fixation powers. The rate of growth and decay of the ability of chlorella to absorb carbon dioxide in the dark after having been exposed to light has been found to be somewhat erratic. The source of this difficulty has been shown to be excess light intensity under anerobic conditions. By making analyses of algae which have fixed carbon dioxide

~~CONFIDENTIAL~~ D

at the conditions of maximum reducing power after illumination, it has been shown that the algae can fix 16 or more times as much carbon dioxide after proper illumination for an hour as they can without this pre-illumination. Longer illumination than an hour without carbon dioxide endangers the life of the chlorella.

After this illumination, the chlorella are analyzed to determine total carbon dioxide activity that has been fixed in the form of plant acids, amino acids and sugars during the period of absorption in the dark with labeled carbon dioxide. A considerable amount of work is in progress on the development of methods for separating these various plant acids. In particular, studies are being made on the separation of aspartic and glutamic acid. It has been found that the ion exchange resin, Dowex 50, does not work; an Amber-light resin IR-4B, is now being tried. A method is being developed for the separation of basic amino acids from neutral amino acids by use of a carboxylated ion exchange resin instead of the standard sulfonic acid resin.

PART D. REPORTED BY W.M. LATIMER

(Project 48B, W.M. Latimer, Director)

Metals and High Temperature Thermodynamics

Gaseous Species at High Temperatures: A successful run has been performed to determine the heat of formation of CN and the relative absorption coefficients of CN and C₂. The results are being calculated.

The vapor pressure of cuprous chloride was determined by a new method which confirms the existence of the trimer molecule, Cu₃Cl₃.

Liquid Metal Systems: A number of determinations of the heat of formation of sodium tin alloys have been carried out in the high temperature calorimeter. The results are being interpreted at present. Samples for study of the Na-U-Bi system by the cooling curve method are being prepared.

Refractories: The apparatus for preparation of TiC, ZrC, CbC, and TaC objects has been completed and tested with a TiCl₄, H₂, and hydrocarbon mixture. The apparatus worked quite well up to about 1200 - 1300°C, but modifications are being incorporated to allow it to be used at higher temperatures.

Thermodynamic Reports: The report on the thermodynamic properties of Pu compounds at high temperatures has been completely revised. The various other thermodynamic reports which are scheduled to be set up in print for publication in the PPR are being brought up to date.

Heat Transfer Problems: A report summarizing the work to date has been written.

Basic Chemistry

Extraction of Uranyl Nitrate into Ether: Several more attempts were made to prepare anhydrous uranyl nitrate for use in the study of its extraction into ether. Since evacuation of the hydrated uranyl nitrate salts resulted in decomposition before dehydration, dehydration was attempted in an ether solution with the hope that the ether molecules would replace the water in the sphere of the UO_2^{++} and prevent decomposition. The hexahydrate was dissolved in ether which had been standing over sodium, and the ether layer was treated in one case with P_2O_5 and in another with $CaCl_2$. After standing a minimum of 8 hours the solution was evaporated in a system open to the atmosphere through $CaCl_2$ drying tubes until crystallization appeared to start. In both cases the solution set into a glass containing a number of crystals with dimensions of the order of 1 mm. The glass was soluble in water unlike the photolysis decomposition product obtained under similar solutions.

Solubility of Pu(IV) -TTA Chelate in 1M $HClO_4$: Measurements of the solubility of the Pu(IV) TTA chelate in 1.000M $HClO_4$ are in progress to determine the various chelation constants between Pu(IV) and TTA. At high concentrations of TTA, c.a. 0.035M, trouble was encountered in making equilibrium measurements of the solubility as the Pu(IV) in solution was being reduced to the +3 oxidation state. It was found that if the solution contained ca. $10^{-4}N$ K_2CrO_7 , the Pu remained in the +4 oxidation state for 8 hours or longer. This was, however, only partially successful as it was found that the solubility was not constant within the limits of error imposed by the analytical process.

The Pu(IV) chelate behaves in aqueous solution like an organic compound insoluble in water. The solid is not easily wet by the perchloric acid and as a result part of the solid floats on the surface of the aqueous perchloric acid and can not be centrifuged easily. Therefore aliquots of the solution containing solid Pu(IV) chelate are centrifuged and then filtered through a platinum filter

stick. Even with these precautions, the solubility as a function of time appeared to fluctuate. However, this variation in solubility which has no trend with time is greater than the error introduced by the technique. Therefore, only an approximate value of the solubility of the solid chelate in 0.03434M TTA and 1.000M HClO₄ can be given. The solubility data under the above conditions fluctuate about the value 4×10^{-8} M. This is an extremely low solubility as this means that 1 ml of this solution contains only about 700 c/m. It should be noted that this solubility is somewhat lower than the tentative solubility which was previously given.

Extraction of Zr(IV) by TTA: Distribution measurements of Zr(IV) between aqueous perchloric acid and benzene TTA solutions have been continued at various perchloric acid concentrations from 2M to 0.2M. Micro amounts of non-radioactive zirconium were used and the zirconium analysis was carried out using the alizarin-calorimetric method. It was found that the zirconium-alizarin lake was slow to form in the case of the analysis of zirconium in the benzene phase, presumably due to slow conversion of the Zr-TTA complex to the lake.

In the experiments run at four acidities from 2.0 M to 0.2M, the hydrogen ion dependence down to 0.4 M was 3.6, meaning an average of 0.4 hydroxide groups per zirconium. At lower acidities the number of hydroxides appears to be increasing to two or three per zirconium. The TTA dependence was rechecked at 2 M perchloric acid and was found to be nearly 4th power, giving four ketones per zirconium in the benzene phase.

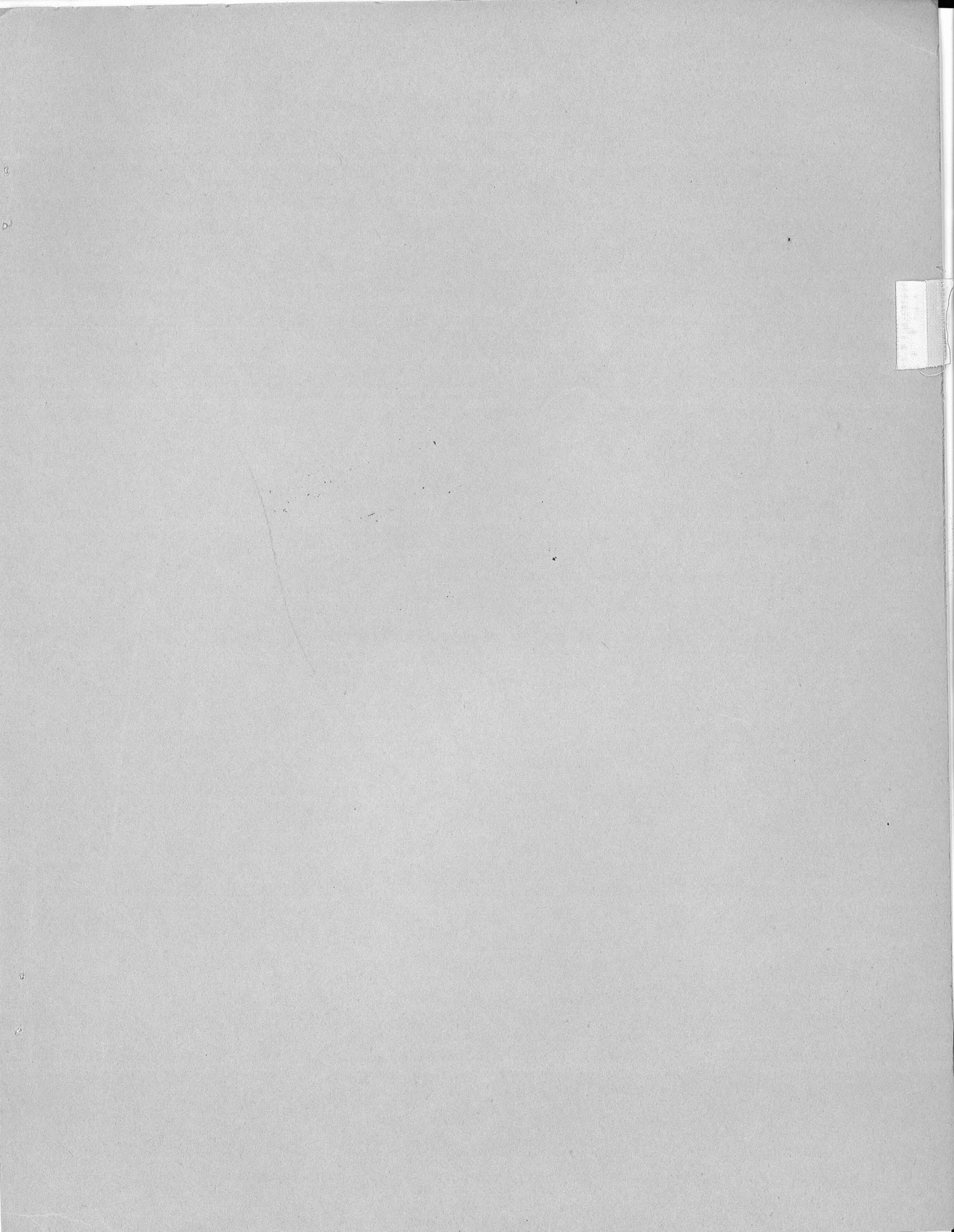
Extraction Experiments with Uranium (VI): Extraction experiments are in progress to determine the distribution coefficient of uranium (VI) between aqueous acid solution and benzene solutions of TTA. The phases are stirred together vigorously and after separation are analyzed spectrophotometrically.

In the initial series of runs, the analyses of the various benzene phases are mostly in error due to the presence of finely dispersed bubbles of the aqueous

[REDACTED]

phase remaining suspended in the light path at the time the measurements were taken. This has been corrected by allowing a longer time for the separation of phases before withdrawing a sample for analysis.

[REDACTED]



~~SECRET~~

DECLASSIFIED

~~SECRET~~