UNCLASSIFIED

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UN CLASSIFIED

ANL-4326(Del.)

UNITED STATES ATOMIC ENERGY COMMISSION

CHEMISTRY DIVISION, SECTION C-1 SUMMARY
REPORT FOR APRIL, MAY, AND JUNE 1949

DELETED VERSION

Classification changed to Unclassified
Authorized by H.F. Carroll 3/14/57
Changed by H. Kinn Date 6-70-12

DELETED VERSION

August 3, 1949

Argonne National Laboratory
Lemont, Illinois

Technical Information Service Extension, Oak Ridge, Tenn.

Photostat Price \$ 6.30

Microfilm Price \$ 3.00

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONFIDENTIAL

TABLE OF CONTENTSPHYSICAL AND INORGANIC CHEMISTRY

Page

Ruthenium Chemistry	4
Isolation of Protactinium	7
Exchange Reactions of Uranium Ions in Solution	7
Heats of Solution of Uranyl Nitrate Hydrates	9
Inorganic Salt-Water-Organic Solvent Systems	13
Lambda Temperatures of He ³ - He ⁴ Mixtures	14
Physical Properties of the Molecular Compound 3ZrCl ₂ · 2POCl ₃	17
Metal Polyuranates	20
Volatility Separations Program	22
Protactinium - Thorium - Uranium Separations by Means of Ion Exchange Resins	27

NUCLEAR CHEMISTRY AND RADIOCHEMISTRY

Spontaneous Fission of U ²³⁶	29
Half-Life and Energy of U ²³⁶	32
Half-Life of Th ²²⁹	35
Alpha Branching of Bi ²¹³	36
Preparation of Thin Samples by Vacuum Sublimation	38

556-002

CONFIDENTIAL

CONFIDENTIAL

4

CONFIDENTIAL

PHYSICAL AND INORGANIC CHEMISTRY

RUTHENIUM CHEMISTRY - P. Wehner and J. C. Hindman

Figures 2 and 3 in ANL-4252, an earlier quarterly report, illustrated the discrepancies among the absorption spectra of various solutions believed to be Ru(IV) in perchloric acid. The solutions had been prepared in the following ways: (1) reduction of ruthenium tetroxide in 1 M HClO₄ by mercurous perchlorate, (2) reduction of ruthenium tetroxide in 11.7 M HClO₄ by hydrogen in the presence of platinized platinum, (3) metathesis of a ruthenium chloride solution with sodium hydroxide and dissolution of the ruthenium hydroxide in perchloric acid, and (4) reduction of ruthenium tetroxide in 1 M HClO₄ by mercury, followed by electrodeposition of mercurous ion. Further work has indicated that none of these methods is a satisfactory means of preparing pure Ru(IV). Dispersion of part of the ruthenium in the colloidal state has been established in the case of methods (3) and (4) and is suspected in the case of method (1). (The extinction of any given solution prepared by method (1) follows Beer's Law, but the extinction coefficients increase with increasing initial concentration of tetroxide used in the preparation.) In the case of method (2) it now appears improbable that such a reduction in 11.7 M HClO₄ will completely reduce the ruthenium to Ru(IV).

A different and more satisfactory method of preparing solutions of Ru(IV) in perchloric acid has been developed: the reduction of ruthenium tetroxide in 9 M HClO₄ by electrolysis at controlled cathode potentials, with platinum electrodes. This method yields solutions that are apparently free of colloidal material and that possess reproducible spectral characteristics. Such solutions were used in the studies described below.

The absorption spectrum of Ru(IV) has been investigated as a function of the perchloric acid concentration. The spectrum in 1 M HClO₄ is shown in Figure 1; that in 0.1 M HClO₄ is nearly identical with this. Increasing perchloric acid concentration intensifies and sharpens the shallow absorption band in the visible region and shifts the wavelength of the maximum towards the ultraviolet. In 6 M HClO₄ the maximum occurs at 475 mμ (molar extinction coefficient, $E_m = 8.1 \times 10^2$) and in 9 M HClO₄ at 472 mμ ($E_m = 8.7 \times 10^2$). On the other hand, increasing perchloric acid concentration tends to obliterate the plateau in the ultraviolet region; in 9 M HClO₄ this plateau is reduced to little more than an inflection point at about 280 mμ.

556-003

The stability of Ru(IV) has been studied as a function of perchloric acid concentration. Solutions in 1 M HClO₄ are quite stable and show no change in absorption spectrum after storage for 40 days at room temperature or 12 hours at 70°C. However, Ru(IV) is slowly oxidized by 6 M HClO₄ at room temperature; spectral changes accompany this process and

CONFIDENTIAL

CONFIDENTIAL

FIG. 1. ABSORPTION SPECTRA OF Ru(III) AND Ru(IV) IN 1 M HClO₄.

556 004

chloride ion appears in the solution. The most noteworthy spectral change is the almost complete transformation of the 475 $m\mu$ band to a plateau extending from 490 to 430 $m\mu$. The spectral changes are apparent after 18 days but are not yet complete after 40 days. At 70°C the oxidation is accelerated and an equilibrium state is reached in 8 hrs in which the ruthenium is in the oxidation state 4.19. Ru(IV) is also unstable in 9 M $HClO_4$ at room temperature; an equilibrium condition is reached within 4 days in which the ruthenium is in the oxidation state 4.24 and Cl^- is present. The spectral changes in the 9 M $HClO_4$ solutions are similar to those in 6 M $HClO_4$.

Studies of the oxidation of Ru(IV) in perchloric acid at controlled anode (platinum) potentials have yielded additional information concerning the formal oxidation-reduction potential of the couple $Ru(IV) \rightarrow RuO_4 + 4e^-$. The new data, together with previously reported values obtained by reduction of ruthenium tetroxide at controlled cathode potentials, are shown in Table 1.

TABLE 1

Formal Oxidation Reduction Potential, E_f , of $Ru(IV) \rightarrow RuO_4 + 4e^-$

$HClO_4$ conc. (M)	E_f from Reduction of RuO_4 (v.)	E_f from Oxidation of $Ru(IV)$ (v.)
1	$-1.40 \pm .05$ (25°C)	$-1.40 \pm .05$ (0°C)
6	$-1.40 \pm .05$ (25°C)	$-1.45 \pm .05$ (0°C) $-1.47 \pm .05$ (25°C)
9	$-1.50 \pm .05$ (25°C)	$-1.51 \pm .05$ (0°C)

Ru(III) has now been successfully prepared by electrolysis at -5°C of Ru(IV) in 6 M $HClO_4$ at controlled cathode (platinum) potentials. The absorption spectrum of freshly prepared Ru(III) is the same in both 1 M and 6 M $HClO_4$ and is reproduced in Figure 1. Ru(III) solutions in 1 M and 6 M $HClO_4$ that are stored at 0°C undergo within 20 hours changes that profoundly affect the absorption spectra. It is believed that these changes are associated with changes in the ionic species of Ru(III). It is possible, however, that they represent slow oxidations to new Ru(IV) species. The changes are being studied in more detail.

Ru(III) is readily oxidized at room temperature by both 1 M and 6 M $HClO_4$; these facts explain the previously noted failure to prepare Ru(III) by electrolytic reduction at room temperature. In 6 M $HClO_4$ the Ru(III) is completely re-oxidized to Ru(IV) within 4 hours; in 1 M $HClO_4$

556 005

CONFIDENTIAL

DECLASSIFIED

the change is complete within 24 hours. At 0°C the rate of oxidation, as judged by the return to the normal Ru(IV) spectrum, is quite low in both acids, and the extent of oxidation is appreciable only after several days.

ISOLATION OF PROTACTINIUM - P. Sellers, R. John and R. Elson

Three additional milligrams of spectroscopically pure protactinium have been isolated from 2 kg of hydroxide residues remaining from previous isolations. The residues contain chiefly Al, Fe, Mn and Zr and lesser quantities of Bi, Cu, Cr, Ga, Mg, La, Ni, Si, Cb, Ta, Ti. The methods used were principally those listed in a previous quarterly report (ANL-4176), namely, carrying on MnO_2 from nitric acid solutions, carrying on insoluble tannates from tartaric acid solutions, and extractions with diisopropyl ketone. In some cases the iron was removed by extraction with ethyl or diisopropyl ether from HCl solution containing a small quantity of oxalate and the manganese from nitrate solution at low acid concentration with ethyl alcohol.

EXCHANGE REACTIONS OF URANIUM IONS IN SOLUTION - E. Rona

Experiments on exchange reactions of uranium in hydrochloric acid solutions have been reported in ANL-4286. The experimental data show that the rate of the exchange reaction of the U(VI) and U(IV) ions is of the first order with respect to the U(VI), second order with respect to the total U(IV) concentration, and minus third order with respect to the hydrogen ion concentration.

To give a reasonable mechanism for this complicated system, it is desirable to know the form of the U(VI) and U(IV) ions in acid solutions. There is strong experimental evidence^{1, 2, 3} that the U(VI) ion is present as UO_2^{+2} , in the absence of complexing agents. More confusing is the evidence as to whether the U(IV) ion is present as U^{+4} or UOH^{+3} in the acid range of the experiments.^{4, 5, 6} Undoubtedly there is a mixture of both. This is substantiated by hydrolysis measurements, from which values of

¹F. Sutton, C.R.C. 325 (1947).

²D. A. MacInnes and L. G. Longworth, MDDC-911 (1948).

³H. W. Crandall, BC-64, (1947).

⁴E. S. Kritchevsky and J. C. Hindman, J.A.C.S. 71, 2096 (1949).

⁵I. M. Kolthoff and W. E. Harris, *ibid*, 68, 1175 (1946).

⁶H. G. Heal, Trans. Far. Soc. 45, 1 and 11, (1949).

CONFIDENTIAL

the equilibrium constant, K_h , for the reaction

have been derived.⁷

To account for the experimental facts, the following mechanism may be proposed:

Rapid, reversible, equilibrium constant K_1 .

Here Y^{+3} is a postulated intermediate complex ion, which may have the following form:

Z_{act}^{+6} is the activated complex in the theory of absolute reaction rates, which breaks down into the final products UOH^{+3} and UO_2^{+2} . Classically, one could regard (3) as a slow reaction, which is followed by the fast reaction

Both viewpoints lead to the same rate expression,

$$V = k (Y^{+3})(UOH^{+3}) \quad (4)$$

Solving (1) for $[UOH^{+3}]$ in terms of $[U(IV)] = [U^{+4}] + [UOH^{+3}]$,

solving (2) for $[Y^{+3}]$, and substituting in (4)

$$V = k K_1 \frac{[U(IV)]^2 [UO_2^{+2}]}{\left[\frac{[H^+]}{K_h} + 1 \right]^2 [H^+]^2} \quad (5)$$

556 007

In expression (5) the activity coefficients are omitted in view of the confusing situation which prevails in the literature in the interpretation of the ionic

⁷K. A. Kraus and F. Nelson, ORNL-23 (1948).

DECLASSIFIED

strength effect of aqueous solutions of strong electrolytes, in the ranges in which the Debye-Huckel theory does not apply.

Substituting for K_h in (5) the value of 0.051 for an ionic strength of 0.25 and a temperature of 25°C, interpolated from Kraus and Nelson's values, the apparent order of the reaction with respect to hydrogen ion over the pH range 0.85 to 1.6 is found to be -3.08. This is in good agreement with the value found in the experiments. The order of the reaction with respect to $[U(IV)]$ and $[UO_2^{+2}]$ given by equation (5) also agrees with the experimental facts.

Other mechanisms may be proposed which would explain the experimental results, such as a third order reaction or dimerization of the U(IV) ion. The first is not considered likely, and there is no experimental evidence for the second.

HEATS OF SOLUTION OF URANYL NITRATE HYDRATES - D. M. Simon and L. I. Katzin

Heat of solution measurements for uranyl nitrate dihydrate and hexahydrate in diethyl ether, ethylene glycol diethyl ether (diethyl "cellosolve"), isobutyl alcohol, and tert-butyl alcohol have been made. The results of these determinations are tabulated below.

TABLE 2

Heats of Solution of Uranyl Nitrate Hydrates in Non-Aqueous Solvents at 25°C. 80 Moles of Solvent per Mole of Solute

Solvent	ΔH_{80}^{25} (kcal/mole)	
	Hexahydrate	Dihydrate
Tert-butyl alcohol	-5.4	2.4
Isobutyl alcohol	-9.6	2.5
Diethyl ether	-2.9	8.8
Ethylene glycol diethyl ether	-0.5	13.2

In the following discussion a general mechanism of solution is presented, and specific mechanisms are formulated for the uranyl nitrate hydrates in the solvents for which heats of solution have been measured.

CONFIDENTIAL
DECLASSIFIED

The formation of undissociated mixed solvates of small coordination number in organic solvents, similar to those observed as crystals in phase studies, are assumed in solution. Uranyl nitrate is considered to be undissociated in the organic solvents, in accord with the following evidence: (1) Kaplan's spectrophotometric studies of uranyl nitrate solutions in acetone; (2) the conductance data for uranyl nitrate in ether solution (A-2903); (3) the apparent consistency of the integral heat of solution of uranyl nitrate dihydrate in isobutyl alcohol over the concentration range 50-95 moles of solvent per mole of solute as observed in this investigation, and (4) the estimated degree of dissociation calculated by Bjerrum's equation. Further, it is assumed that there is only one mixed solvate form in a given solution, and that at least two molecules of water remain attached to this final product. Although the degree of correspondence of the formalism with reality is unknown, it is interesting to note that all but one of the specific solvates predicted by this method have been previously isolated by Katzin and Sullivan.

It is assumed that the following reaction occurs on solution of uranyl nitrate dihydrate:

The integral heat of solution is given by:

$$Q_f \text{ UN} \cdot 2\text{H}_2\text{O} \cdot n\text{S}(\text{l}) - Q_f \text{ UN} \cdot 2\text{H}_2\text{O}(\text{c}) - nQ_f \text{ S}(\text{l}) = \Delta H_{i2\text{H}_2\text{O}}$$

$$\Delta H_{i2\text{H}_2\text{O}} = n\Delta h$$

where the symbols have the following meanings:

$\Delta H_{i2\text{H}_2\text{O}}$ = integral heat of solution of dihydrate at 25°C and a mole ratio of 80:1.

n = number of molecules of solvent forming mixed solvate with the dihydrate.

Δh = unit heat of reaction per mole of solvent reacting

Q_f = heat of formation

S = solvent

UN = uranyl nitrate

555 809

DECLASSIFIED

For the hexahydrate the analogous equations are:

$$Q_f \text{UN}.(6-y)\text{H}_2\text{O}(\text{c}) - Q_f \text{UN}.6\text{H}_2\text{O}(\text{c}) + y Q_f \text{H}_2\text{O}(\text{l}) = \Delta H_1$$

$$Q_f \text{UN}.(6-y)\text{H}_2\text{O}.n'\text{S}(\text{l}) - Q_f \text{UN}.(6-y)\text{H}_2\text{O}(\text{c}) - n' Q_f \text{S}(\text{l}) = \Delta H_2$$

$$\Delta H_{16\text{H}_2\text{O}} = \Delta H_1 + \Delta H_2$$

$$\Delta H_2 = n'\Delta h$$

where

$$\Delta H_{16\text{H}_2\text{O}} = \text{integral heat of solution of hexahydrate at } 25^\circ\text{C and } 80:1.$$

n' = number of solvent molecules in mixed solvate formed from the hexahydrate.

In the above equations it may be noted that the heat of solution of water freed from the hexahydrate in the uranyl nitrate-organic solution has not been included. Preliminary experiments in one solvent indicate that the effect is negligible; however, more precise and comprehensive experiments are in progress. The use of Δh above implies that there is a constant (within the accuracy of the present method) heat of reaction of uranyl nitrate per solvent bond formed regardless of the number of water molecules attached to the uranyl nitrate.

To determine $\underline{n}$ and $\underline{n}'$, values of the heats of dehydration are required. These may be calculated from the heats of solution of the hydrates in water. It is assumed that the mechanisms of solution of the three hydrates in water differ only by a preliminary hydration reaction and that the degree of ionization is constant. The difference in the heat of solution of the hexahydrate and dihydrate (previously reported in ANL-4286) is then, the heat of dehydration of the hexahydrate to the dihydrate. Similarly the difference in the heats of solution of the hexahydrate and the trihydrate is the dehydration of the hexahydrate to give trihydrate. The values of ΔH_1 obtained for these dehydrations from the heats of solution of the three hydrates are used to determine $\underline{n}$ and $\underline{n}'$. The ΔH values are given below.

The ΔH_1 value is chosen so that the n/n' ratio is nearest the ratio of small integral numbers. Determination of n and n' for solution of the uranyl hydrates in tert-butyl alcohol is illustrated below.

$$\Delta H_{12H_2O} = n\Delta h = 2.4$$

$$\Delta H_{16H_2O} = \Delta H_1 + n'\Delta h = -5.4$$

$$\text{With } \Delta H_1 = -7.22, \frac{n}{n'} = \frac{2.4}{1.8} = \frac{4}{3}$$

$$\text{With } \Delta H_1 = -10.9, \frac{n}{n'} = \frac{2.4}{5.5}$$

$\Delta H_1 = -7.22$ gives the better n/n' ratio. Therefore a specific mechanism of solution may be formulated for tert-butyl alcohol, as follows:

Table 3 gives the result of similar considerations for the other solvents.

TABLE 3

Mechanism of Solution of Uranyl Nitrate Dihydrate and Hexahydrate in Organic Solvents

Solvent	ΔH_1 (kcal/mole)	n/n'	Δh (kcal/mole)	$\underline{n}$	$\underline{n'}$
Isobutyl alcohol	-10.9	2.5/1.3	1.25	2	1
Diethyl ether	- 7.2	8.8/4.3	4.4	2	1
Ethylene glycol diethyl ether	- 7.2	13.2/6.7	6.6	2	1

Specific mechanisms for the other solvents are:

isobutyl alcohol

556 011

DECLASSIFIED

diethyl ether

ethylene glycol-diethyl ether

All underlined mixed solvates have been isolated in the solid state in the phase studies of Sullivan and Katzin.

The reason for formation of $\text{UN.2H}_2\text{O.IBA}$ instead of $\text{UN.2H}_2\text{O.2IBA}$ (or the more reasonable $\text{UN.3H}_2\text{O.IBA}$) when the hexahydrate dissolves in isobutyl alcohol is not understood. In all cases except isobutyl alcohol the coordination number of the product in solution is independent of the solid dissolved.

INORGANIC SALT-WATER-ORGANIC SOLVENT SYSTEMS.

COBALTOUS NITRATE PHASE STUDIES - L. I. Katzin and J. Ferraro

With acetone as the organic component, phase studies have shown solids which are the hexahydrate, the tetrahydrate, and what seems to be a three-and-a-half-hydrate, as well as the trihydrate which is known from the cobaltous nitrate-water system. There seems to be no mixed solvate, at 25°C, down to the level of the trihydrate. The evidence for mixed solvates below this hydration is incomplete.

With tertiary butyl alcohol as the organic component, the phase system shows the following solid solvates: hexahydrate, tetrahydrate-monoalcoholate, and probably trihydrate-trialcoholate, dihydrate-dialcoholate, and anhydrous trialcoholate.

SPECTROPHOTOMETRIC STUDIES - L. I. Katzin and E. Gebert

A report is being prepared for publication dealing with the complexes of cobaltous ion and nitrate ion in organic solvents, and the water relations, which indicate that the complexes are probably of the six-coordination type, the positions unoccupied by nitrate ion being occupied by water or organic groups.

Studies have been initiated on the behavior of cobaltous chloride in organic solvents.

556 012

DECLASSIFIED

LAMBDA TEMPERATURES OF He³ - He⁴ MIXTURES - B. M. Abraham,
B. Weinstock, and D. W. Osborne

It has been shown⁸ by comparing the isothermal flow of liquid He³ and of liquid He⁴ through a small channel or superleak that no superfluid flow occurs in pure He³, at least down to 1.05°K. These experiments have been extended to mixtures of He³ and He⁴ in order to study the feasibility of concentrating He³ by means of a superleak and to determine the effect of composition on the lambda temperature.

The first experiment was made in an attempt to separate the He³ from approximately 10 cc of a mixture containing 92.1% He³ and 7.9% He⁴. Subsequently, experiments were made with 2.4% He³ and with mixtures prepared by diluting a portion of the 92.1% He³ with He⁴.

The He³ - He⁴ mixture was condensed in the capillary tube leading to the platinum-glass superleak used previously,⁸ which was immersed in a bath of ordinary liquid helium whose temperature was regulated by pumping. The rate of isothermal flow through the superleak was then determined at successively lower temperatures by observing the rate of pressure rise in a large volume on the exit side of the leak. The starting material, the portion which flowed through the leak during the course of the measurements, and the residuum were analyzed by means of a mass spectrograph.

With the 92.1% He³ it was found that the rate of flow decreases monotonically as the temperature is lowered to 1.05°K, and it is therefore concluded that the lambda temperature of this mixture is lower than 1.05°K. With pure He⁴, as well as with the other mixtures tested, the curve of flow rate versus temperature rises sharply below a temperature which is characteristic of the liquid. With pure He⁴ this rise begins at the lambda point, 2.19°K, and hence the point at which the sharp rise begins is considered to be the lambda point of the mixture. The breaks in the curves for the mixtures were located with an estimated uncertainty of 0.05°K.

The lambda temperatures determined in this way and the mass spectrographic analyses are given in Table 4.

TABLE 4
Lambda Temperatures and Composition Changes of
He³ - He⁴ Mixtures, as Observed in Superleak Experiments

Mole % He ³			λ-Pt. (°K)
Starting material	Effluent	Residuum	
2.4	0.32	8.2	2.04
10.7	2.7	13.8	1.92
20.3	-	-	1.63
28.2	10.9	43.7	1.56
92.1	91.0	93.6	<1.05

⁸D. W. Osborne, B. Weinstock, and B. M. Abraham, Phys. Rev. 75, 988 (1949).

It is believed that there was little change in composition until the temperature was reduced below the lambda point of the mixture, so that the lambda temperatures tabulated correspond to the composition of the starting material.

In Figure 2 the experimental lambda temperatures are plotted against composition, along with a curve calculated by J. W. Stout.⁹ This calculation is based on the model proposed by Taconis, Beenakker, Nier, and Aldrich¹⁰ to account for their measurements of the relative concentrations of He^3 and He^4 in the liquid and in the vapor in equilibrium with it. They assume that He^3 - He^4 solutions are perfect, both above and below the lambda point, except that below the lambda point the He^3 is soluble in the normal fraction of the He^4 and insoluble in the superfluid fraction of the He^4 . The agreement between Stout's calculated curve and the experimental points is within the estimated experimental error.

It is seen from Table 4 that large changes in He^3 concentration can be effected by isothermal flow through a superleak at temperatures below the lambda point of the mixture. A slight change in concentration will occur even above the lambda point if the amount of gas above the liquid on the entrance side of the leak is appreciable. Since the concentration of He^3 is higher in the vapor phase than in the liquid,¹⁰ the liquid flowing through the leak, even without fractionation by superfluid flow of He^4 , has a lower He^3 concentration than the starting material. This effect is sufficient to account for the concentration change observed with the 92.1% He^3 but is far too small to account for the changes observed with the other mixtures.

The limit of He^3 concentration attainable by any of the various methods of separation^{11, 12} which depend on the superfluid flow of liquid He^4 and the lack of superfluid flow of He^3 can be predicted approximately from Figure 1. Thus, the concentration limit at a temperature of 1.8°K is about 14% He^3 , and the limit at 1.5°K is about 30% He^3 .

It is planned to extend these measurements to lower temperatures obtained by adiabatic demagnetization, and to measure the He^3/He^4 ratio of the material as it issues from the superleak by means of a mass spectrograph directly connected to the apparatus.

⁹J. W. Stout, to be published in Phys. Rev.

¹⁰K. W. Taconis, J. J. M. Beenakker, A. O. Nier, and L. T. Aldrich, Phys. Rev. 75, 1966 (1949).

¹¹J. G. Daunt, R. E. Probst, and S. R. Smith, Phys. Rev. 74, 495 (1948).

¹²C. A. Reynolds, H. A. Fairbank, C. T. Lane, B. B. McInteer, and A. C. Nier, Phys. Rev. 76, 64 (1949).

Fig. 2. Lambda temperatures of He^3 - He^4 mixtures. Points determined with a superleak. Curve calculated (see text).

556 015

DECLASSIFIED

PHYSICAL PROPERTIES OF THE MOLECULAR COMPOUND $3\text{ZrCl}_4 \cdot 2\text{POCl}_3$ -
D. M. Gruen and J. J. Katz

Continued interest in the separation of hafnium and zirconium by the fractional distillation of complexes between the tetrachlorides of these elements and phosphorus oxychloride has prompted further investigation of these compounds.

In a previous report, (ANL-4286) it was pointed out that chemical analyses of the zirconium complex led to the formula $3\text{ZrCl}_4 \cdot 2\text{POCl}_3$ (molecular weight = 1006) which is at variance with the formula $2\text{ZrCl}_4 \cdot \text{POCl}_3$ advanced by van Arkel and de Boer¹³ as well as with the formula $\text{ZrCl}_4 \cdot 2\text{POCl}_3$ cited by Sugden.¹⁴ It was hoped that further work would give more insight into the constitution of the complex.

Attempts to obtain x-ray diffraction patterns have failed since the complex up to the present has been obtained only in an amorphous condition.

The value 32 for Trouton's constant obtained from vapor pressure data (see ANL-4286) indicated the highly associated nature of the complex in the liquid state. In addition, measurements of the freezing point depression of the material in hexachlorobenzene gave a molecular weight of 3000, showing that the substance exists as a trimer in solution.

The surface tension of the zirconium complex was measured by the method of differential capillary rise, and was found to be 27.6 dyne centimeter⁻¹ at 338°C. Liquid densities of the compound were measured in a closed, precision-bore capillary dilatometer and the value found at 338°C was 1.76 gm/cm³. Values at other temperatures are listed in Table 5. From the surface tension and density data, one may calculate the parachor by means of the well known formula

$$P = \frac{M}{D} \gamma^{\frac{1}{4}}$$

The parachor value thus found is 1308. The value calculated on the basis of 217.6 units for each phosphorus oxychloride molecule and 268 units for each zirconium tetrachloride molecule in the complex is 1240. The experimental result therefore is 68 units too high. We would like to suggest that this represents additional evidence for association in the liquid state, since positive parachor anomalies are often found in connection with fused salt systems where association is known to occur.¹⁵

¹³A. E. van Arkel and J. H. de Boer, Z. für anorg. Chem. **141**, 289-296 (1924).

¹⁴F. B. Garner and S. Sugden, J. Chem. Soc. Part I, 1298 (1929).

¹⁵S. Sugden, "The Parachor and Valency," p. 178 (1930).

556 016

DECLASSIFIED

TABLE 5

Liquid Densities of $3\text{ZrCl}_4 \cdot 2\text{POCl}_3$

Temperature (°C)	244	293	318	373	404	438
Density (g/cm ³)	1.922	1.838	1.805	1.709	1.688	1.636

Vapor density measurements were carried out in an all-quartz system, employing a Bodenstein type quartz spiral pressure gage as a null manometer.¹⁶ This was necessary because the vapors of the complex are reactive toward mercury. Values obtained at various temperatures are listed in Table 6.

TABLE 6

Vapor Densities of $3\text{ZrCl}_4 \cdot 2\text{POCl}_3$

Temperature (°C)	327	332	344	377	394	437
Density relative to air = 1 at the particular temperature and pressure	13.9	13.0	10.5	8.05	7.88	7.75
Molecular weight of vapor	400	374	302	232	227	223

Assuming that the complex dissociates in the vapor phase according to the equation

one finds that at 318°C dissociation is 29% complete while at 377°C it is 85% complete. Further studies of this equilibrium are in progress.

556 017

¹⁶We wish to acknowledge the cooperation of Dr. Dwight Hutchison who suggested and constructed the quartz spiral gage.

DECLASSIFIED

METAL POLYURANATES - H. R. Hoekstra and J. J. Katz

Magnesium Diuranate - The previously reported data (ANL-4286) on the thermal decomposition of magnesium diuranate, with formulas revised slightly in accordance with further data, may be summarized as follows:

A. In vacuum:

B. In air:

The two steps in the decomposition of MgU_2O_7 were found to be reversible. Peculiarities in the initial stages of the oxygen absorption curves of $\text{MgU}_2\text{O}_{5.94}$ and $\text{MgU}_2\text{O}_{6.64}$ (i.e., more rapid absorption) remained to be explained. The suggestion that the initial rapid oxygen absorption (in the regions $\text{MgU}_2\text{O}_{5.94}$ to $\text{MgU}_2\text{O}_{6.08}$ and $\text{MgU}_2\text{O}_{6.64}$ to $\text{MgU}_2\text{O}_{6.68}$) were due to reaction at the surface of the solid, and that the remainder of the oxygen absorption curve was determined by diffusion of the gas through the crystal lattice, was found to be incorrect, since pulverizing the solid did not appreciably increase the extent of the initial rapid reaction rate. Further investigation indicates that these are regions of solid solution. X-ray pictures taken at the extremes of the $\text{MgU}_2\text{O}_{5.94}$ - $\text{MgU}_2\text{O}_{6.08}$ range showed only one phase to be present in each instance, a fluorite structure similar to UO_2 .

Oxygen absorption by $\text{MgU}_2\text{O}_{5.94}$ was found to occur at temperatures as low as 185°C , the final composition after about 7 hrs at this temperature being $\text{MgU}_2\text{O}_{6.03}$. At 300°C , the composition reached $\text{MgU}_2\text{O}_{6.05}$ in 4 hrs, and at 400°C reached $\text{MgU}_2\text{O}_{6.09}$ in 2.5 hrs. As a result of these experiments

it appears that the decomposition of MgU_2O_7 may be divided into the following regions:

Barium Diuranate - The results on thermal decomposition of barium diuranate obtained to date may be summarized as follows:

A. In vacuum:

B. In air:

A sample of BaU_2O_7 placed in an evacuated system will begin to liberate oxygen at $\sim 750^\circ\text{C}$, and continue to do so as the temperature is increased until the composition $\text{BaU}_2\text{O}_{6.86}$ is reached. At the present time it is impossible to say whether this is a true reversible process. The solid can be converted to the diuranate at 800°C , by heating for several hours with an excess of oxygen, but the reaction is extremely slow when the stoichiometric amount of oxygen is used. Further work is required before this question can be settled. An approximate value for the heat of the reaction, 75 Kcal/mole, has been obtained.

A sample of $\text{BaU}_2\text{O}_{6.86}$ heated in an evacuated system will begin to liberate oxygen at 875°C (0.5 mm) but the maximum pressure obtainable as the temperature is increased, rises very slowly (10.0 mm at 1125°C). As the temperature is lowered from 1125°C , absorption of oxygen is rapid, but the "equilibrium" pressure obtained as the temperature was being increased is not reached. In addition, if the system is pumped out for a few seconds, the pressure obtained at any temperature is lower than the previously determined value for that temperature. Evacuation of the system at 1100°C for twenty minutes leaves a solid having the composition $\text{BaU}_2\text{O}_{6.64}$, as determined by measuring the oxygen absorbed to reconvert to the diuranate. Conversion to $\text{BaU}_2\text{O}_{6.86}$ is rapid, being nearly complete within five minutes at 500°C , but, as mentioned previously, the remaining oxygen is absorbed very slowly, even at 800°C .

A sample of BaU_2O_7 heated to 1400°C in air showed evidences of having been at least partially fused. Decomposition had occurred at the melting point, since bubbles could be observed in the solidified melt. The formula of the oxide which is stable at this temperature could not be determined since oxygen was undoubtedly absorbed during cooling.

Another sample of BaU_2O_7 has been heated to 1500°C in vacuum by induction. The product was a black powder, but here again it was impossible to determine the formula directly, since there was evidence of volatilization of a portion of the uranium either as UO_3 or less likely as a barium-uranium oxide. An attempt will be made to determine the formula of the black residue by measuring the oxygen absorbed on reconversion to the diuranate.

VOLATILITY SEPARATIONS PROGRAM - Irving Sheft, Harry Andrews and J. J. Katz

For the most part, previous work on volatility methods has been directed toward the complete separation of uranium, plutonium, and fission products from each other by utilizing differences in the volatility of various compounds (i.e., fluorides, chlorides, etc.) of these substances. The high temperature vapor phase reactions which have hitherto been considered pose serious equipment problems; problems attendant upon collection of the products of fractional sublimation have received relatively little attention, but are obviously formidable.

The present work has the more modest goal of removing uranium from irradiated metal in a form which can be readily decontaminated, leaving a relatively non-volatile residue of plutonium and fission products which can then be decontaminated and separated by conventional methods. The uranium compound which seems most suitable for this purpose is the hexafluoride, UF_6 , which has been shown by previous workers to be readily purified by fractional distillation. It seems desirable to convert irradiated uranium to UF_6 under the mildest conditions in order to minimize the spread of plutonium and fission products in a difficultly collectable form throughout the apparatus. For this purpose liquid phase fluorination is of particular interest. Liquid phase fluorinating reagents are sufficiently powerful so the reactions can be made to go under very mild conditions; all of the reaction products are then present in solution or suspension in the liquid phase. After reaction is complete, the liquid phase may be removed from the reaction vessel by pumping or gravity to a distillation column where the volatile UF_6 may be stripped from the non-volatile plutonium and fission product fluorides. Liquid phase fluorinating agents which seem of most interest are indicated in Table 8.

TABLE 8
Reagents of Interest in Liquid Phase Fluorinations

	B.P. ($^\circ\text{C}$)	M.P. ($^\circ\text{C}$)
BrF_3	130	8.8
BrF_5	~ 40	-61.3
IF_5	98	9.6
ClF_3	12	-83

556 021

DECLASSIFIED

It also appears possible to carry out liquid phase fluorinations with certain of these reagents in the presence of diluents such as fluorocarbons, anhydrous hydrogen fluoride, or uranium hexafluoride itself. In these systems, the solubility relationships may be such as to suggest other separations methods in addition to distillation.

General Observations on Fluorination with Bromine Trifluoride -

The present work has until now been primarily concerned with liquid phase reactions of bromine trifluoride. The behavior of a considerable number of substances has been examined qualitatively. Since bromine trifluoride can be handled conveniently in quartz, these reactions were studied by introducing a small amount of the given substance into a quartz tube containing BrF_3 (liq). After several hours, and a short period of refluxing under helium, the BrF_3 was removed by distillation in vacuum and the residue examined. Identification of the compounds was usually by x-ray, although in general the x-ray patterns were rather poor because of the low temperature of preparation. The results are summarized in Table 9.

Of particular interest is the fact that massive uranium metal reacts smoothly with BrF_3 (liq) at room temperature. Increasing the temperature until the BrF_3 refluxes increases the rate considerably, so that it appears possible to achieve a desired rate of reaction by temperature control. The uranium oxides all react more vigorously than the metal, whereas the lower uranium fluorides appear to react faster than the metal but more slowly than the oxides.

From Table 9 it is seen that a number of oxides (i.e., ZrO_2 , ThO_2) do not react at an appreciable rate with BrF_3 (liq). Since on thermochemical grounds all oxides should react with BrF_3 (liq) the failure of some oxides to show significant reaction must be attributed to kinetic considerations. A procedure has been devised which seems to have general applicability in preparing fluorides by liquid phase fluorination from normally unreactive oxides. This consists in coprecipitating a mixed oxide with uranium, molybdenum, or other oxide which forms a volatile or BrF_3 -soluble fluoride. Thus, by treating a mixed zirconium-uranium oxide with BrF_3 , ZrF_4 identified by x-ray and by sublimation is readily obtained. The same technique has also been successful in preparing NpF_4 and PuF_4 , since NpO_2 and PuO_2 both react slowly with BrF_3 (liq).

Behavior of Neptunium and Plutonium Compounds with BrF_3 (liq).

A New Preparation of Plutonium(IV) Fluoride - The behavior of plutonium and neptunium with BrF_3 (liq) is of importance from the point of view of whether volatile fluorides are formed. A number of experiments were performed in a quartz apparatus in such a manner that any volatile neptunium or plutonium would be caught in a series of cold traps. The contents of the traps were hydrolyzed and examined for activity. In the case of

TABLE 9

Reactions of Bromine Trifluoride with Various Substances

Reactant	Reaction*	Product (by x-ray analysis)**
Ru pellet	+	$\text{RuF}_5(?)$
Zr	-	---
Cb	+++	CbF_5
Th	-	---
U	++	UF_6
Ce	+	$\text{CeF}_3(?)$
Pr	+++	PrF_3
Mo	+++	MoF_6
MoO_3	++	MoF_6
WO_3	++	WF_6
Cb_2O_5	++	CbF_5
U_3O_8	++	UF_6
UO_2	++	UF_6
ThO_2	-	---
ZrO_2	-	---
$\text{U}_3\text{O}_8 + \text{ZrO}_2$	++	ZrF_4
UF_4	+	UF_6
UF_3	+	UF_6
NpF_3	+	NpF_4
NpO_2	+	NpF_4
NpO_2	+	Amorphous
PuO_2	+	$\text{PuO}_2\text{F}_2^{***}$
$\text{PuO}_2 + \text{U}_3\text{O}_8$	++	PuF_4
$\text{Pu}(\text{IO}_3)_4$	++	PuF_4
$\text{Th}(\text{IO}_3)_4$	++	ThF_4
$\text{Th}(\text{CO}_3)_2$	++	ThF_4

*+indicates a slow reaction; ++, a rapid smooth reaction; and +++, vigorous reaction with flame; - indicates no observable reaction after 12 hours.

**Through the courtesy of Dr. W. H. Zachariasen.

***This is a new compound which is isomorphous with NpO_2F_2 .

plutonium, no activity was detected in the traps even under conditions where reaction with the formation of PuF_4 was shown to occur. In the case of neptunium, in one experiment approximately 10 per cent of the original activity was found in the cold trap. The absence of a volatile plutonium fluoride may be a consequence of the use of quartz apparatus, which may reduce any PuF_6 which forms. It is possible that in properly treated metal apparatus and with the use of stronger fluorinating agents such as ClF_3 , volatile PuF_6 may be collected under conditions appropriate for the collection of UF_6 . Since the question of volatile plutonium compounds under the fluorination conditions contemplated here has a most important bearing on the proposed volatility separations process, this point will be more intensively studied.

Plutonium dioxide does not appear to react completely with $\text{BrF}_3(\text{liq})$ even on refluxing; a mixture of PuO_2 and U_3O_8 formed by coprecipitation and ignition yields PuF_4 . In one experiment, PuO_2 yielded the new compound PuO_2F_2 (by x-ray analysis). This material was insoluble in water, however, and it appears likely that the PuO_2F_2 existed only as a surface layer.

In the course of this work, a new synthesis for PuF_4 has been worked out which appears to have some advantages, at least for small scale preparations, in comparison to the conventional high temperature hydrofluorination procedure. This synthesis involves the reaction of plutonium(IV) iodate with $\text{BrF}_3(\text{liq})$. Plutonium(IV) iodate is highly insoluble and readily prepared from Plutonium(IV) solutions. It has the further advantage that it is easily obtained anhydrous. The reaction is carried out in a quartz apparatus; after the initial reaction subsides, the bromine trifluoride is refluxed and all of the volatile matter is then removed by distillation in vacuum. The residue is heated to 100° to assure complete removal of BrF_3 , and the product is obtained as a green, glassy solid. Because of the low temperature of preparation, x-ray methods were not very satisfactory, and the product was therefore characterized by direct chemical analysis.

Fluorine was determined by distillation as H_2SiF_6 , collected in slightly basic solution, and titrated with standard thorium nitrate solution using sodium alizarin sulfonate as indicator. Known fluorine samples showed recoveries greater than 99 per cent. The residual solution was then assayed for plutonium radiochemically. The results of the analysis are as follows:

Volume of Original H_2SO_4 Solution	=	100 cc
Pu Sample	=	10 μl
Pu: c/m/sample	=	5114 c/m; 5185 c/m
Total μgm	=	726
Total μmoles	=	3.03
Fluorine: Found, μgm	=	233
μmoles	=	12.27
F/Pu Ratio	=	4.05

The F/Pu ratio of 4.05:1 indicates that substantially pure PuF_4 is obtainable in this way. In addition to the iodate, the phosphate, arsenate, molybdate, and other anions which yield volatile fluorides should also be useful. It has also been found possible to obtain anhydrous ThF_4 from $\text{Th}(\text{IO}_4)_4$ (see Table 9).

We wish to acknowledge with thanks the cooperation of the Analytical Group and particularly Mrs. Rosanna Hospelhorn for the fluorine analyses.

Decontamination of Irradiated Uranium Metal with Liquid Phase Fluorination - One experiment with pile irradiated uranium has been run. A 100 mg sample of uranium metal was irradiated in the Argonne CP-3 pile for 24 hours, and allowed to cool for 2 weeks. At the end of this cooling period the sample showed an activity of 1 r at 1 cm. The sample was introduced into a quartz reaction vessel to which was attached a set of U-tubes. BrF_3 was added from a nickel dropping funnel, and the reaction mixture refluxed for several hours until all of the uranium was in solution. The system was then evacuated, and UF_6 , Br_2 , and volatile fission products collected in the cold-trap. The distillate and residue were removed from the line, hydrolyzed, and analyzed. The results are given in Tables 10 and 11.

The data in Tables 10 and 11 are due to the Analytical Group of Chemical Engineering Division. Our thanks are due to Mr. H. Hyman for aid in interpreting the results.

TABLE 10
Gross Decontamination Factors

	Residue	Distillate	Remarks
U (mg)	1.05	114	Loss in residue ~1%
Pu (c/m)	6.5×10^3	~100*	Loss in distillate 0-10%
Total γ ($\mu\mu\alpha$ **) (6/17/49) ⁺	560	48	Gross γ decontamination factor ⁺⁺ ~13
Total β (c/m) (6/17/49) ⁺	6.3×10^7	3.3×10^6	Gross β decontamination factor ⁺⁺ ~20
Total γ ($\mu\mu\alpha$ **) (6/29/49) ⁺	420	6	Gross γ decontamination factor ⁺⁺ ~70
Total β (c/m) (6/29/49) ⁺	4.0×10^7	7.7×10^5	Gross β decontamination factor ⁺⁺ ~50

*The actual count on the plate was 5 c/m., the uranium background was 60 c/m.

** In arbitrary ionization units.

+The distillation was carried out on 6/16/49. The activity in the distillate has about a 3 day half-life.

++Residue activity/distillate activity.

556 025

DECLASSIFIED

TABLE 11
Fission Products in Distillate

Fission Product	Total c/m (upper limit)	% activity in distillate as of 6/17/49	Minimum decontamination factor
Ru	$1 \times 10^3 \beta$	0.03	5×10^4
Ce	$5 \times 10^3 \beta$	0.15	1×10^4
Zr	$2 \times 10^3 \beta$	0.06	3×10^4
Cb	25 γ	0.4	250

It can be seen that even the crude distillation performed in this experiment yields encouraging results. It should be possible to obtain better decontamination factors by more efficient distillation, and suitable apparatus for this purpose is actively under investigation. The short cooling period probably accounts for much of the residual activity in the distillate. It appears to arise from the short lived fission products I, Te, Mo, and from U^{237} . The fission products which were analyzed for were present in only negligible amount in the distillate (Table 11).

In this experiment, no attempt was made to separate UF_6 and bromine, which is the other product of the BrF_3 reaction in U metal. Since UF_6 and Br_2 have boiling points close to each other, a separation by distillation may be difficult. It has been found that ClF_3 reacts rapidly with Br_2 (in BrF_3) to give BrF_3 and Cl_2 . The separation of UF_6 , Cl_2 and BrF_3 is almost certainly simpler, and a procedure wherein ClF_3 is added to remove bromine has the added advantage of using ClF_3 as the primary source of fluorine for the uranium fluorination, with BrF_3 playing the role of a fluorine carrier.

PROTACTINIUM - THORIUM - URANIUM SEPARATIONS BY MEANS OF ION EXCHANGE RESINS - James C. Sullivan, Martin H. Studier and Eileen C. Janda

The use of the cation exchange resin Dowex 50 for the separation of protactinium and thorium (ANL-4286) has been studied in more detail. Distribution coefficients were determined for protactinium, thorium, and uranium in various concentrations of hydrochloric acid and mixtures of hydrochloric acid and sodium chloride. These batch experiments indicated that protactinium could be eluted very readily without appreciably moving the thorium; however, when column runs were attempted the protactinium could not be eluted in a reasonable length of time but seemed to adhere in a narrow band at the top of the column.

The batch data for 0.5 M hydrochloric acid and varying concentrations of sodium chloride gave a straight line dependence of distribution coefficients as a function of chloride ion concentration in the region from 1.0

to 6.0 molar total chloride. In the same concentration range, using hydrochloric acid, discontinuities were observed at about 3.0 molar and at 4.5 molar hydrochloric acid. These data suggest that in the region of the discontinuities oxygen atoms are being stripped from the protactinium.

Thorium - protactinium solutions to which hydrofluoric acid had been added to the point of precipitation of ThF_4 were equilibrated with Dowex 50 resin. Essentially no protactinium was absorbed by the resin, but when such a solution was passed through a column all the protactinium was absorbed and could not be eluted.

A series of batch experiments were performed with the anion exchange resins IRA-400, Dowex A-1, and SAR-A-2. Distribution coefficients were determined for protactinium and uranium in oxalate, tartrate and citrate solutions at various concentrations and for thorium, uranium, and protactinium in hydrochloric acid solutions. The results of all these experiments indicated that any of the above mentioned complexing agents could be used for separation of protactinium, thorium and uranium. The hydrochloric acid system, first suggested by K. A. Kraus and G. E. Moore (ORNL-329,330), was given the most attention. Distribution coefficients were determined for all three resins at 0.2 M thorium chloride in varying concentrations of hydrochloric acid and at 8.5 M hydrochloric acid with varying concentrations of thorium. The Dowex A-1 seemed to be slightly better than the other two, but since it is not commercially available it was decided to use the IRA-400. At constant thorium concentration the distribution coefficient,

$$K_d = \frac{\text{weight absorbed}}{\text{grams of resin}} \times \frac{\text{ml of solution}}{\text{weight in solution}}$$

for protactinium increased from about 8 at 2 M hydrochloric acid to 210 at 8.5 M hydrochloric acid. At higher acid concentrations thorium precipitates. The distribution coefficient for thorium is essentially zero. Uranium is absorbed very well but separation from protactinium can be made by elution with some overlapping of the two elution curves. The concentration of thorium affects the distribution coefficient protactinium quite markedly. With the hydrochloric acid concentration kept constant at 8.5 M the K_d varied from 210 at 0.2 M thorium to 18 at 1.0 M thorium.

A "dummy" column run was made using 6 grams of thorium oxide which had been irradiated in the thimble of the Argonne CP-3 pile for four days. The thorium oxide was dissolved in 8.0 M HCl using a trace of hydrofluoric acid as a catalyst. The resulting solution (~ 0.2 M in thorium) was run through an IRA-400 resin column which had been pretreated with 8.0 M hydrochloric acid. The protactinium was absorbed in a narrow band at the top of the column and essentially all the thorium passed through. The thorium was decontaminated from fission products by a procedure developed by D. F. Peppard (ANL-WMM-497). The thorium was extracted into pentaether, and the fission products were washed out with 8.0 M ammonium nitrate.

DECLASSIFIED

556 027

A sample of oxide containing 0.8 gram of ionium which had been irradiated for one month at Hanford was dissolved and passed through a IRA-400 column. The solution was ~ 0.2 M in thorium and 8.0 M in hydrochloric acid. The column was then washed with 8.0 M hydrochloric acid to remove traces of ionium. The protactinium and uranium (U^{232} formed by $Pa^{231} (n, \gamma) Pa^{232} \rightarrow U^{232}$) were quantitatively adsorbed and did not contain a detectable amount of ionium.

Work is still in progress to determine the optimum conditions for eluting protactinium and uranium from the IRA-400 resin.

NUCLEAR CHEMISTRY AND RADIOCHEMISTRY

SPONTANEOUS FISSION OF U^{236} - A. H. Jaffey and A. Hirsch

Counting has been continued on the larger sample described in the last quarterly report. In addition, the samples have been analyzed with a mass spectrograph by M. Inghram, giving better values for the isotopic content. The revised concentrations are shown in Table 12.

TABLE 12

Composition of Enriched U^{236} Samples

	Sample I	Sample II
U^{235}	$59.1 \pm 0.20\%$	$54.7 \pm 0.24\%$
U^{236}	22.2 ± 0.25	22.1 ± 0.30
U^{238}	18.6 ± 0.25	23.2 ± 0.30

With the concentrations known accurately, the samples were most conveniently "weighed" by means of neutron-induced fission counting of the U^{235} , assuming that U^{236} has a zero slow neutron fission cross-section. A standard was prepared by H. Diamond from enriched U^{235} (97%), by electroplating. The uranium was ignited and weighed as U_3O_8 . However, some uncertainty remains as to the amount of impurity in the uranium standard, and this uncertainty is reflected in the weights of the two U^{236} -containing samples.

In the "weighing" technique, the neutron-induced fission counts were determined in a paraffin block containing a Ra-Be source. The counting rates were determined as a function of the pulse-height selector bias down to the point at which alpha-particles were counted, and the plateau extrapolated to zero bias. A correction of a few per cent was then made for the fission particles which were completely absorbed in the sample. Table 13 shows the results of these measurements.

556 028

DECLASSIFIED

Using the technique described in the last quarterly report, the spontaneous fission counting was continued, with the results shown in Table 13. As before, corrections have been made for the spontaneous fission rates of U^{238} ($\lambda_x = 24.8 \text{ f/g/hr} \pm 4\%$) and U^{235} ($\lambda_y = 1.3 \text{ f/g/hr} \pm 46\%$). The spontaneous fission rate (f/g/hr) of U^{236} , λ_z , was calculated from the equation

$$\lambda_z = \frac{1}{R_z} \left(\frac{C}{m} - R_x \lambda_x - R_y \lambda_y \right)$$

where R_x , R_y , R_z are the fractions (Table 12) present of U^{238} , U^{235} and U^{236} , respectively, C = counting rate (f/g/hr), and m = total weight of uranium (g).

The errors (standard deviation) were evaluated by the usual statistical methods. Because of the small number of counts observed, these methods do not apply accurately but will serve to indicate the magnitude of the errors. The absolute error in λ_z is almost entirely due to the large fluctuations occurring at low counting rates.

TABLE 13

Spontaneous Fission of U^{236}

	Sample I*	Sample II
Wt. U^{235} (from counting neutron-induced fissions)	$0.56 \pm .03 \text{ mg}$	$1.215 \pm .60 \text{ mg}$
Wt. total uranium	$0.95 \pm .05 \text{ mg}$	$2.22 \pm .11 \text{ mg}$
Wt. U^{236}	$0.211 \pm .011 \text{ mg}$	$0.49 \pm .024 \text{ mg}$
Total spontaneous fission measured	7	25
Corrected to zero bias and for absorption in sample	7.26	27.3
Total time elapsed	536 hours	1404 hours
Spontaneous fissions expected from U^{238}	2.35	17.9
Spontaneous fissions expected from U^{235}	0.39	2.2
Net fissions attributed to U^{236}	4.52	7.2
Spontaneous fission rate for U^{236} in f/g/hr	40 ± 24	10 ± 8

*These are the same data reported previously, but recalculated with the new percentage values.

556

29

DECLASSIFIED

The value from Sample I may be somewhat high, since two-thirds of the data were taken with only a cadmium shield, which was not as effective as the boron carbide shield later used to decrease the absorption of cosmic-ray neutrons by the U^{235} in the sample.

The effectiveness of the boron shield was determined in the following manner. It was first necessary to determine the counting rate of an unshielded U^{235} sample due to cosmic-ray-neutron-induced fission. This counting rate was too low to be determined with the amount of U^{235} that could be used in the ionization chamber, and so BF_3 was used as a stand-in. The relative efficiencies of the BF_3 counter and a U^{235} sample for absorbing neutrons was determined by exposing them both to high neutron fluxes of known ratio. An enriched BF_3 proportional counter containing a known amount of B^{10} was placed in a paraffin block. The counting rate (neutrons absorbed per second) was determined with a 25 mg Ra-Be neutron source placed next to the paraffin block. The ionization chamber used for spontaneous fission counting was then placed in the same paraffin block, with an enriched uranium sample of known U^{235} content in it. The absorption of neutrons by the U^{235} sample was determined by counting the fission pulses with a 1 gm Ra-Be neutron source placed in the position previously occupied by the 25 mg source. After correcting for the neutron source sizes, the ratio of the counting rate (i.e., neutron absorption) of the BF_3 counter to that of the ionization chamber containing the U^{235} sample was found to be 850. This ratio can be calculated theoretically from the amounts of B^{10} and U^{235} used and the known thermal neutron cross-sections, with the assumptions that (1) the absorption cross-sections of U^{235} and B^{10} are completely proportional to $1/v$ or that the neutrons in the paraffin block were completely thermalized, (2) both the U^{235} and the B^{10} were exposed to the identical flux, and (3) there was no self-absorption in either samples. Although none of these assumptions are exactly correct, the calculation was made and found to give the ratio 1500. This is satisfactory agreement in view of the fact that the boron counter actually absorbed a large fraction of the neutrons penetrating it (tending to decrease the effective neutron flux), and in view of the effect of the U^{235} resonances in a neutron flux which was far from completely thermalized.

The unshielded BF_3 counter, within a paraffin block, but with no neutron source present, was found to count at the rate of 1.0 c/m due to cosmic-ray neutrons. Assuming cosmic-ray neutrons have the same energy-distribution as the Ra-Be-paraffin neutrons, the U^{235} sample would be expected to count (due to absorption of cosmic-ray neutrons) $1.0 \times 1/850 = 1.18 \times 10^{-3}$ c/m with no neutron shield. The ionization chamber containing the U^{235} sample was then exposed to the 1 gm Ra-Be neutron source with and without the boron carbide shield around the chamber. The boron-carbide shield was found to cut the counting rate by a factor of 400. Thus, the U^{235} sample would be expected to give $1/400 \times 1.18 \times 10^{-3} = 2.9 \times 10^{-6}$ cosmic-ray-neutron-induced fissions per minute when protected by the shield. This corresponds to 1 count in 240 days (5760 hours). The U^{236} enriched Sample II contained less U^{235} than the standard

556 30

DECLASSIFIED

used in these measurements, and hence could be expected to have about 1 count in 430 days. This value is an upper limit, since the cosmic-ray neutrons are of lower energy than the Ra-Be neutrons used in the experiment, and hence would be expected to be more easily absorbed by the boron-carbide shield.

With the present sample, the limits of error will be decreased only as the square root of the counting time, since the chief source of uncertainty is the random fluctuations of the counting rate. Table 14 shows the calculated value for λ_z as a function of counting time. Considerably greater accuracy would be possible if the U^{238} fraction were smaller, since the expected fluctuations in the U^{238} counting rate greatly increase the expected fluctuations of the U^{236} counting rate. For a given U^{236} percentage, the greatest accuracy could be obtained if the U^{235}/U^{238} ratio were inversely as the specific spontaneous fission rates, i.e., $24.8/1.3 = 19$.

TABLE 14

Variation of the Measured Specific Spontaneous
Fission Rate with Counting Time

Counting time (hours)	Counts measured	Counts corrected for absorption, etc.	λ_z	$\pm \sigma_{\lambda_z}$
185	2	2.18	- 5	± 17
637	9	9.8	2	± 11
976	14	15.3	2.7	± 8
1404	25	27.3	10	$\pm 8^*$

*This value is the same as the previous one because the counting rate is larger, so that despite the smaller relative error, the absolute error is about the same.

HALF-LIFE AND ENERGY OF U^{236} - A. H. Jaffey, J. Mech and H. Diamond

The U^{236} samples used for the spontaneous fission counting (see above) were analyzed with the 48 channel pulse analyzer¹⁷ in order to measure the specific alpha activity of the U^{236} . The results reported here are preliminary, since the absolute determinations of the weights of uranium in the sample are not complete.

¹⁷Ghiorso, Jaffey, Robinson, Weissbourd, CC-3887; AECD-2508; PPR, Vol. 14B, No. 16.8.

The pulse analyses showed two constituents with approximately equal activities - U^{234} at 4.76 Mev and U^{236} at 4.48 Mev. Although the samples were fairly thick, the resulting straggling effect was minimized by collimating the emitted alpha-particles. The remaining low-energy asymmetric straggling due to source thickness was allowed for by successive approximations, assuming the shape of the low-energy part of the U^{234} peak to be approximately the same as that of the U^{236} peak, and by assuming the high energy part of the U^{236} peak to be similar to that of the U^{234} peak.

The U^{238} and U^{235} activities present were not identifiable in the pulse analyzer curves. The U^{238} activity (4.2 Mev) was quite low and was lost in the low energy tail of the U^{236} peak. The U^{235} activity was approximately 10% of the U^{236} activity, and presumably consists of two peaks. Although only the lower energy peak (4.4 Mev) has ever been directly observed,¹⁸ the observation¹⁹ of a gamma-ray associated with U^{235} and pulse-analyses by Clark et al proves that another peak exists at about 4.56 Mev. The 4.4 Mev peak presumably contains 80% of the U^{235} activity. Because of the small U^{235} alpha-activity, and because of the relatively large straggling resulting from sample thickness, both U^{235} peaks were lost under the U^{236} peak (4.48 Mev). The U^{235} activity was calculated from the known weight present, using Nier's half-life value.¹⁹

Five curves were determined on each of Samples I and II. The results are tabulated in Table 15. The results of the pulse analyses gave the fraction of the total activity due to each constituent. The total alpha activity was then measured in a 2π ionization chamber for alpha-counting. Gain plateaus were measured and extrapolated to the gain at which tube noise counted. The pulse level at this gain is very small, and only a small fraction of the alphas were not counted. The counting efficiency at this extrapolated gain was taken as 52%.

The average value of the half-life was found to be 2.75×10^7 years. This may be compared to the value²⁰ 2×10^7 years previously determined from a yield estimate of the U^{236} content of a neutron-bombarded U^{235} sample (so-called CW-3), and a crude pulse analysis of the U^{235} and U^{236} peaks. In view of the low concentration of U^{236} in the latter sample and the difficulty of yield estimation, the agreement is good.

The energy of the U^{236} peak was measured in the pulse analyzer using as standards: U^{234} , Pu^{239} , Po^{210} , Pu^{238} . The energies of the standards were taken as: U^{234} , 4.763 Mev;¹⁸ Pu^{239} , 5.14 Mev;²¹ Pu^{238} , 5.49 Mev;²¹ Po^{210} , 5.30 Mev.¹⁹

¹⁸ Clark, Spencer-Palmer, Williams, Br-522.

¹⁹ References in Seaborg and Perlman, Rev. Mod. Phys., 20, 585-667 (1948).

²⁰ For references see Seaborg and Perlman, "Tables of Isotopes" BC-59, May, 1947 (Secret)

²¹ Jesse and Forstat, Phys. Rev. 73, 926 (1948).

TABLE 15

Specific Activity of U^{236}

	Sample I	Sample II
U^{236} (per cent by weight) #	22.2 ± 0.25	22.1 ± 0.30
U^{235} (per cent by weight)	59.1 ± 0.20	54.7 ± 0.24
U^{238} (per cent by weight)	18.6 ± 0.25	23.2 ± 0.30
U^{236} (per cent of total activity) *	48.9 ± 1.2	45.2 ± 0.9
U^{234} (per cent of total activity) *	45.3 ± 1.2	50.8 ± 1.1
U^{235} (per cent of total activity) **	5.4	4.1
Total alpha activity (c/m) ***	$27,000 \pm 50$	$70,100 \pm 100$
U^{236} alpha activity (c/m)	$13,200 \pm 320$	$31,690 \pm 630$
U^{236} disintegration rate (d/m) ****	$25,380 \pm 620$	$60,940 \pm 1,220$
Wt. of U^{236} (mg)	$0.211 \pm .008$	$0.491 \pm .020$
Specific activity U^{236} (d/m/mg)	$120,300 \pm 5,600$	$124,100 \pm 5,500$
Half-life of U^{236} (years)	$(2.79 \pm .13) \times 10^7$	$(2.71 \pm .12) \times 10^7$
Average value	2.75×10^7 years	

Determined by M. Inghram (see previous section).

* From pulse analysis.

** Calculated from known content and half-life.

*** Measured in 2π ionization chamber and counting rate extrapolated to minimum pulse size.

**** Calculated using 52% as counting efficiency.

Sample I, being the thinner of the two samples, was used for the energy measurement. To minimize effects of sample thickness, the alpha-particles were sharply collimated. The range of U^{236} alpha-particles should be approximately 11 mg/cm² in U_3O_8 . Since the average sample thickness was 0.075 mg/cm², the displacement of the U^{236} peak due to sample self-absorption should be roughly .02 Mev. However, the internal standard, U^{234} , should be displaced by the same amount. Since the position of the U^{234} peak is the most important in locating the U^{236} peak position (the other standards serving primarily to determine the slope of the energy versus pulse-height line), the sample thickness should introduce no important error.

The average of eight determinations using the standards in various combinations was $4.478 \pm .020$ Mev⁺. This agrees quite well with a previous determination (4.5 Mev) measured on the CW-3 sample mentioned above.

*to here
Measured ↓*

HALF-LIFE OF Th^{229} - French Hagemann

In CB-3692, on the basis of a single experiment, the half-life of Th^{229} was reported as 7000 ± 2000 years. In order to reduce the uncertainty of this value, several more determinations have been made. Briefly, the method of determination was the following. Known amounts of purified U^{233} were allowed to decay for a measured time. The Th^{229} daughter activity was isolated either by a series of coprecipitations with zirconium iodate or by direct extraction from 0.1 N nitric acid solution with 0.25 M thenoyltrifluoroacetone solution in benzene followed by 0.1 N nitric acid washes. The total alpha activity of the purified material was measured and corrected for chemical yield and for RdTh^{228} alpha particles (from the small amount of U^{232} impurity present in the U^{233}). The $\text{Th}^{229}/\text{RdTh}^{228}$ ratio was determined with the pulse analyzer. The chemical yield was determined by adding a known amount of UX_1 tracer to the U^{233} solution and measuring the yield of UX_1 beta activity.

The results of the determinations are summarized in Table 16.

TABLE 16

Half-Life of Th^{229}

Sample No.	U^{233} α counts/min.	Th^{229} α counts/min.	Decay time, (days)	Th^{229} Half- life, (years)
09 - 19*	3.1088×10^7	3860	489	7477
09 - 26	2.2189×10^7	3807	697	7712
09 - 27	1.2403×10^7	3637	1114	7212
09 - 30	2.3844×10^7	4501	741	7452
09 - 31	1.2833×10^7	3981	1158	7086
09 - 32	2.3822×10^7	4763	743	7055
09 - 33	1.2878×10^7	3905	1160	7262
09 - 34	1.2159×10^7	2299	746	7489

*Determination reported in CB-3692

⁺Average deviation

555 034

DECLASSIFIED

The mean value of the half-life from the eight determinations is 7,343 years with an average deviation from the mean of 189 years.

ALPHA BRANCHING OF Bi^{213} - French Hagemann and J. Mech

Bi^{213} (NpC), the 47 minute daughter of U^{233} , which decays chiefly by beta-emission, exhibits some alpha branching analogous to the "C" products in the natural radioactive series. The extent of this alpha branching was previously reported as 4% in CB-3692. A more thorough redetermination of the branching ratio has given a value of 2% which is in agreement with that found by the Canadian workers (CRC-269).

The bismuth activity was separated from a stock solution of Ac^{225} either by electroplating directly upon a platinum disc or by precipitating with lead sulfide carrier, followed by removal of the lead as sulfate and mounting of the supernatant solution.

The ratio of the number of alpha particles in the small peak at 5.86 Mev due to Bi^{213} and the large peak at 8.34 Mev due to Po^{213} (the 3.2×10^{-6} second product of Bi^{213} beta decay) was measured by means of the pulse analyzer. The geometry of the instrument was varied according to the amount of alpha activity present by placing brass collimating discs of varying thicknesses honeycombed with vertical 1/16" diameter holes over the sample. A background of chamber and collimator contamination was measured immediately before or after placing each sample in the chamber. This background was subtracted from the observed alpha spectrum. An additional correction of considerable magnitude for straggling of the Po^{213} peak in the region of the Bi^{213} peak was applied. The amount of this correction was determined by interpolating from the low energy Po^{213} α particles on both sides of the Bi^{213} peak.

The previously reported value of 4% had not been corrected for Po^{213} straggling. Applying a rough correction for this effect gives a value of 2.8%.

The results of the measurements are summarized in Table 17.

CONFIDENTIAL

PREPARATION OF THIN SAMPLES BY VACUUM SUBLIMATION - W. Thiel

A vacuum sublimation apparatus for preparing thin samples for alpha range determinations has been devised and is now working satisfactorily. The apparatus is shown in Figure 3. Basically the device consists of a metallic crucible containing the material to be sublimed which is heated by electron bombardment. Resting in the mouth of the crucible is a plug containing an orifice which to some extent collimates the vapor to a receptor plate which is cooled by liquid N_2 . The apparatus is flexible in that various types of conducting crucibles can be used depending upon the ultimate temperatures desired. Temperature gradients can be controlled by adjusting the electron distribution from variously shaped filaments. The orifice plug is maintained considerably hotter, ca. $200^\circ C$, than the bottom of the crucible. The temperature is measured by means of an optical pyrometer sighted on the bottom of the crucible.

When tungsten crucibles are used they should be heated in vacuo for several hours at $2000^\circ C$ in order to remove volatile constituents in the metal. Ca, Mg, Al, Be, Cr, Cu, Fe, Mn, Pb, Sr, Ti are all evolved slowly in microgram quantities.

In order to recover material not deposited on the receptor plate a quartz mask and mantle are provided. When $RaCl_2$ was evaporated ($>1100^\circ C$ but $<1500^\circ C$) it was observed that the rest of the equipment was quite uncontaminated. The quartz pieces were easily cleaned with dilute HF.

The radiant flux from the orifice is sufficient to melt stellite receptor plates, and so it is advisable to evaporate over a very short time interval when polished metal plates are used and a high temperature is needed. Traces of oxygen due to leaks or inadequate outgassing will discolor stellite plates although the deposit is still invisible and the mirror surface is unimpaired. Apparently quartz plates are quite useful in that they do not warp or craze.

CONFIDENTIAL

556-037

DECLASSIFIED

TABLE 17

Alpha Branching of Bi^{213}

Sample No.	Geometry of Collimator	Total counts of Bi^{213}	% alpha branching	
			Corrected for background	Corrected for background and Po^{213} straggling
833-16	5.8%	950	2.64*	1.93
833-17	5.8%	620	3.65*	2.69
	5.8%	565	3.55*	2.43
	5.8%	340	2.73*	2.09
	5.8%	303	2.73*	2.03
	5.8%	531	2.50*	1.91
833-18	0.12%	477	2.88	1.92
	0.46%	205	2.40	1.76
833-19	0.07%	268	2.42	1.79
	0.12%	188	2.04	1.47
	0.46%	336	2.28	1.54
	1.02%	228	2.46	2.23
	3.15%	384	3.11	2.19
833-20	5.8%	3,954	2.68	1.84
	no collimator 50%	10,493	3.0	2.43
Mean				2.02%
Average deviation from mean				0.26%

*Uncorrected for background, which was very low.

DECLASSIFIED

556 - 636

CONFIDENTIAL

556-038

FIG. 3. VACUUM SUBLIMATION APPARATUS.

CONFIDENTIAL

DECLASSIFIED