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MASTER

**THERMODYNAMIC STUDIES ON
HEAVY ELEMENTS AND STUDIES IN
NUCLEAR CHEMISTRY**

for the period

February 1967 to January 1968

A.E.C. Contract AT (11-1)-1716

Department of Chemistry

Purdue University
Lafayette, Indiana

January 1968

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Thermodynamic Studies on Heavy Elements and
Studies in Nuclear Chemistry

Annual Report

COO-1716-4

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January 1, 1968

Edited by

J. W. Cobble

for the

U. S. Atomic Energy Commission

Department of Chemistry
Purdue University
Lafayette, Indiana

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I. Introduction

This report contains information and summaries of the research activities carried out under contract AT(11-1)-1716 from February 1, 1967 to December 31, 1967. During this period three Ph.D. theses were completed and a number of manuscripts prepared for publication; abstracts of these are included in this report.

Some of the work reported in this summary is of a preliminary nature and should not be referred to without permission of the project director.

II. Research Activities

A. Nuclear Fission Research

1. Ternary Fission of U^{238} Induced by Intermediate Energy He^4 Ions (Iyer)

Further evidence has been obtained for the existence of ternary fission in which a heavy excited nucleus divides into three fragments of comparable size from radiochemical studies on U^{238} bombarded with 20-120 MeV He^4 ions. The work reported herein is a continuation of that given in the previous annual report C00-347-28. The absolute formation cross sections for Na^{24} , Mg^{28} , Si^{31} , S^{38} , Ca^{47} , Mn^{56} and Ni^{60} in the 39 ± 1 MeV He^4 ion induced fission of U^{238} clearly establish the transition region between binary and ternary processes, the "cross over" occurring around $A = 47$. The corresponding data for Ta^{183} , Ta^{184} and upper limits for Au^{198} , Pb^{208} and Pb^{212} also clearly indicate the absence of any possible highly asymmetric binary fragments.

The fission product nature of the light ternary fragments was confirmed by the forward-backward recoil properties at various (40-120 MeV) energies. A recoil range of 12.00 ± 0.43 mg/cm² in Uranium has been obtained for Mg^{28} which corresponds to a kinetic energy of about 45 ± 5 MeV. Sr^{88} , a typical binary fission product also showed nearly identical ranges and recoil properties in Uranium.

The measured binary fission cross sections were corrected for independent yields based on CCR rule and using an appropriate value of ν (number of neutrons boiled off) for each mass split, calculated from the total mass-energy balance. (ν has been found to decrease with

increasing mass asymmetry). The corrected cross sections are given in Table I and are summarized in Figure 1. The mass distribution clearly indicates absence of any structure in the ternary ($A = 24$ to $A = 47$) region suggesting a statistical type of ternary process accompanying a statistical type of binary process.

Table I
Fission Product Cross Sections
Fission of U^{238} by 39 MeV He^4 Ions

<u>Fission Product</u>	<u>Total Isobaric Chain Yield</u>
Na^{24}	230 ± 110 nanobarns
Mg^{26}	200 ± 50 "
Si^{31}	60 ± 30 "
S^{36}	25 ± 6 "
Ca^{47}	≤ 5.0 "
Mn^{56}	400 ± 100 "
Ni^{66}	29 ± 6 microbarns
Ta^{183}	1.6 ± 0.8 "
Ta^{184}	300 ± 155 nanobarns
Au^{199}	≤ 5 "
Pb^{209}	≤ 4 "
Pb^{212}	≤ 13 "

Figure 1.

Mass Yield Curve for U^{238} Irridiated with 39 MeV
 He^4 Ions.

The excitation function for formation of Mg^{28} and the ratio of $\sigma_{\text{Mg}^{28}}/\sigma_{\text{total}}$ binary fission (Figure II) in the range of 20-120 MeV show that the ternary fission process changes sharply with energy, particularly below an excitation energy of 20 MeV. It is thus highly unlikely that such light fragments can be observed at lower excitation energies. These conclusions are consistent with the previously reported lack of evidence for possible thermal neutron induced ternary fission of U^{235} and spontaneous ternary fission of Cf^{252} , but are inconsistent with the claims to the contrary based on purely instrumental measurements. This work is being submitted to the Physical Review for publication.

2. Ternary Fission of U^{238} Induced by Intermediate Energy He^3 Ions (MacMurdo)

Work was begun on the first complete mass yield curve for the fission of natural uranium induced by 32 MeV He^3 ions. Absolute cross sections were determined radiochemically for approximately 35 binary and ternary fission products including seven rare earth isotopes. Rigorous radiochemical schemes were worked out for the separation of several extremely low-yield fission products such as Ta^{183} , Re^{183} and Au^{199} from gross fission product solutions.

The use of low-background, high efficiency Geiger counters allowed the determination of absolute cross sections as low as 3 nanobarns (e.g., Ca^{47}) which is roughly seven orders of magnitude lower than the cross sections of the highest yield fission products.

Figure 2.

The Ratio of the Mg^{28} Cross Section to the Total Binary
Fission Cross Section For U^{238} Irradiated with 20-120 MeV
 He^4 Ions.

Thus far Na^{24} , Mg^{28} , Si^{31} and S^{38} have been isolated as ternary fission products. A systematic search for possible complementary fragments such as Au^{198} , Pb^{208} and Pb^{212} is being conducted with no measurable activities yet detected. All bombardments were carried out on the 60-inch cyclotron at Argonne National Laboratory for lengths of times between one and three hours. Each target assembly contained roughly 200 mg. of natural uranium foil. When catcher foil techniques were required, either Ag foils (99.9999% pure) or Al foils (99.999%) were used depending on the particular isotope desired. Blank foils were included when necessary. The preliminary data obtained to date are summarized in Figure 3.

3. Ternary Fission of Th^{232} Induced by Intermediate Energy He^4 Ions (Roginski)

Following the discovery of ternary fission by Iyer and Cobble a study of the ternary fission of various heavy element isotopes was undertaken in this laboratory. This report covers the work on U^{235} and Th^{232} to date.

The cross sections for the production of Mg^{28} from U^{235} and Th^{232} with He^3 and He^4 were determined. These cross sections and those reported previously for U^{238} are all the same, within one standard deviation of 150 nanobarns. Similar results were noted for the production of S^{38} for which the cross sections are all the same, within one standard deviation of 15 nanobarns, for U^{235} , Th^{232} and U^{238} . From these results it can be concluded that the ternary fission-ability parameter is not a sensitive function of Z and A over the short range of isotopes studied.

Figure 3

Mass Yield Distribution For U^{238} Irradiated with
32 MeV He^3 Ions.

A more detailed study of the ternary fission mass yield curve of Th^{232} with He^4 has been started. This system was chosen for study because it forms the same compound nucleus as U^{235} plus neutrons which has been studied instrumentally by Muga with thermal neutrons. A series of light isotopes were chosen: Na^{24} , Mg^{28} , Si^{31} , P^{32} , P^{33} , S^{38} , K^{42} , K^{43} , Ca^{47} , Sc^{47} , Sc^{48} , and Sc^{49} . To date the cross sections for Na^{24} , Mg^{28} , Si^{31} , S^{38} , and an upper limit for Ca^{47} (1.4 nanobarns) have been determined.

In a comparison of the results obtained with earlier work by Muga, several discrepancies are noted. In the data which have been obtained, there is no sign of a peak in the vicinity of mass 32 as has been postulated by Muga from instrumental studies of ternary fission. In comparing the system of Th^{232} bombarded with 45 MeV He^4 with the system of U^{235} bombarded with thermal neutrons, the coulomb barrier for the alpha particle must be considered. Once the compound nucleus, U^{238*} , has been formed, the probability of its fissioning into binary or ternary modes will be independent of the reaction by which it was formed; but it will depend on the excitation energy of the system. A comparison of the ratio of ternary fission/binary fission for the two systems will, therefore, eliminate the effect of the coulomb barrier. The effects of the centrifugal/^{barrier} will be very small for intermediate energy alpha particles. Since the ratio of ternary fission to binary fission has been found to rise rapidly with energy, the ratio of ternary fission/binary fission of Th^{232} with 45 MeV He^4 must be higher, by several orders of magnitude, than the ratio of ternary fission/binary

fission for U^{235} with thermal neutrons. It can be concluded that the cross sections for ternary fission obtained by Muga must be too high by several orders of magnitude. The radiochemical studies of the U^{235} irradiated with thermal neutrons support this conclusion.

Several models have been proposed for binary fission charge distribution. From those models proposed, the two which appear to be most applicable to binary fission at intermediate energies are the equal charge ~~distribution~~^{displacement} model and the ~~equal~~^{constant} charge ratio model. A study of the independent yields of P^{32} , K^{42} , Sc^{47} and Sc^{48} has been initiated in order to determine which of these theories, if any, is applicable to ternary fission. Because of the very neutron rich isotopes which would be produced in the case of the equal charge ratio model in such light isotope regions, the isotopes studied will be produced in very small quantities by this model (1 nanobarn for P^{32} and less for the others). Measurable amounts (about 10 nanobarns for P^{32} and 0.7 for K^{42}) would be produced in the equal charge distribution model.

4. Ternary Fission Studies on Bi^{209} Induced by Intermediate Energy He^4 Ions (Uhl)

Since the Z^2/A parameter plays an important role in binary fission it is of interest to see if similar parameters have some role in ternary fission. To this end, the fission of bismuth and plutonium is ^{being} studied with intermediate energy alpha particles and the light fragments resulting from ternary fission (i.e. magnesium, calcium, sulfur, sodium, etc.) will be isolated radiochemically.

Very pure bismuth targets have been made. These were prepared by vacuum evaporation of 99.9999% pure bismuth and resulted in self-supporting foils of 20-30 milligrams/cm² bismuth.

The (α ,xn) cross sections of bismuth for 45 MeV alpha particles total about one barn. These reactions produce large amounts of astatine which decay to polonium. All are alpha emitters and should initially be removed quantitatively from solution in a glovebox.

The work thus far has been directed toward the solution of this problem. A bismuth target was bombarded with 45 MeV alpha particles for only 3 microampere hours. Chemical separations were performed with the intent of eliminating and isolating all alpha activity and then proceeding to the radiochemical separation of Mg²⁸, Ca⁴⁷ and Sr⁸⁹. The alpha emitters were separated in the first two steps of the chemical procedure and no alpha activity was found in further precipitates. Less than 0.5 cpm of Ca⁴⁷ and Mg²⁸ were found when the samples were placed in the low-level counters. The Sr⁸⁹ was approximately 66 cpm.

Future plans call for bombarding a target for 30 microampere hours at the same energy to determine if any ternary products can be obtained at this energy, also noting the increase of total activity and alpha activity resulting from a ten fold increase of current. Further experiments will probably include use of higher energy alpha particles to obtain more reasonable yields of ternary fission products.

5. Fission Studies on Iridium (Brodzinski)

The fission resulting from the helium ion bombardment of naturally occurring Ir^{191, 193} was studied radiochemically and by a plastic fission track technique. Thin targets were prepared by vacuum evaporation of iridium metal onto silver and aluminum foils, and absolute cross sections were determined for the production of eleven nuclides from fission induced by 42.2 MeV helium ion bombardments. The excitation function was determined by measuring the total fission cross section at thirteen different energies. Individual fission products were purified, and their activities were measured using low background beta counters. Decay curves and theoretical treatment of the Γ_f/Γ_n data were resolved by computer programmed least squares analyses.

The mass distribution (Figure 4) was observed to be symmetric with a full width at half maximum of 27 ± 2 mass units. The average number of neutrons emitted per fission event was 2 ± 1 neutrons. The total fission cross section was found to be 45 ± 11 microbarns. The value of the fission level density parameter was found to be approximately given $A/10$, and the ratio of A_f/A_n was found to be 1.18. The fission threshold was determined to be 22.3 ± 0.7 MeV. (Figure 5). This work has been submitted for publication in the Physical Review.

6. Excitation Functions for the Helium-Ion Induced Fission of Rhenium, Lutetium and Thulium (Raisbeck)

This work was completed and published in Phys. Rev., 152, 1270 (1967).

Figure 4

Mass Yield Curve for the Fission of Indium Induced
by 42.2 MeV Helium Ions.

Figure 5

**Absolute Total Fission Cross Sections for the
Fission of Natural Iridium Induced by He^4 Ions.**

7. The Fission of Rhenium by Intermediate Energy Helium Ions (Mennings)

This work was published in Phys. Rev., 153, 1294 (1967).

B. General Nuclear Research

1. Radiochemical Searches for Polymeric Neutrons (MacMurdo and Brodzinski)

Searches for polymeric neutrons were concluded for the time being with negative results. The hypothetical reactions used were $\text{Be}^9(t, n_2)\text{B}^{10}$, $\text{Fe}^{56}(\alpha, n_2)\text{Ni}^{58}$ and $\text{Fe}^{56}(\alpha, n_4)\text{Ni}^{58}$ for the production of the species and the hypothetical reactions $\text{Al}^{27}(n_2, p)\text{Mg}^{28}$ and $\text{Al}^{27}(n_4, p2n)\text{Mg}^{28}$ were assumed for the detection reactions. Table I is a summary of the limits for the various parameters which were obtained from a number of experiments. In general, these data provide a more rigorous search for the n_2 and n_4 bound states than published to date. The detection method assumes that the capture cross section for n_2 and n_4 are at least as large as 10 microbarns.

Table I.

Parameters for Polymeric Neutrons

	<u>Dineutron</u>		<u>Tetraneutron</u>
	Be target	Fe target	Fe target
Lifetime (sec)	$<1.2 \times 10^{-11}$	$<1 \times 10^{-11}$	$<1 \times 10^{-10}$
Production Cross Section(habobarns)	<0.44	<80	<8
Polymeric Neutrons/Incident Bombarding Particle	$<4.2 \times 10^{-13}$	$<9 \times 10^{-11}$	$<9 \times 10^{-12}$

This work is being written up for publication.

C. Physical-Inorganic Research

1. The Thermodynamic Functions of Np(V) and Np(VI) (Brand)

This work has been completed and submitted for publication. An abstract of the paper follows, and has been issued as report CCO-1716-1.

The solubility and heat of solution of $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ have been measured giving values for the free energy and heat of solution of $-2,940 \text{ cal mol}^{-1}$ and $5,060 \text{ cal mole}^{-1}$, respectively. Estimation of the entropy of $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as $123.4 \text{ cal mole}^{-1} \text{ deg}^{-1}$ then fixes the entropy of $\text{NpO}_2^{++}(\text{aq})$ as $-20 \pm 2 \text{ cal mole}^{-1} \text{ deg}^{-1}$. The heat of reduction of $\text{NpO}_2^{++}(\text{aq})$ to $\text{NpO}_2^+(\text{aq})$ by hydrogen peroxide was found to be $-10,310 \text{ cal mole}^{-1}$ and E^0 for the $\text{NpO}_2^{++}/\text{NpO}_2^+$ couple was measured as -1.130 volts. These data permit calculation of the entropy of $\text{NpO}_2^+(\text{aq})$ as $-11 \pm 2 \text{ cal mole}^{-1} \text{ deg}^{-1}$. By comparison of the E^0 for the $\text{NpO}_2^{++}/\text{NpO}_2^+$ electrode and the formal potential reported elsewhere, corrections could be estimated for adjusting the $\text{UO}_2^{++}/\text{UO}_2^+$, $\text{PuO}_2^{++}/\text{PuO}_2^+$ and $\text{AmO}_2^{++}/\text{AmO}_2^+$ formal potentials to true E^0 values. These were found to be -0.057 v , -0.907 v and -1.594 v , respectively.

2. The Heat of Solution of Plutonium Metal and the Entropy of Pu(III) (Hinchey)

This work has been completed and submitted for publication. An abstract of the paper follows, and has been issued as report CCO-347-27.

The heat of solution of pure α -phase plutonium metal has been measured in 6.03 M and 2.0 M HCl, giving values of -139.4 ± 0.8 and -139.2 ± 0.8 Kcal/mole, respectively. The heat of solution of $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}$ (c) has been measured as -8.056 ± 0.032 Kcal/mole. This value, together with measurements of the solubility of PuCl_3 (c) and reasonable estimates of the activity coefficients leads to a value of -47 ± 3 eu for the entropy of $\text{Pu}^{+3}(\text{aq})$.

3. The Entropies of the Trivalent Lanthanide and Actinide Ions (Hiechey)

This work has been completed and is being written up for publication. The data are summarized in report COO-347-27.

III. Personnel

Dr. James W. Cobble, Project Director
Dr. Richard J. Hinchey, Research Assistant
Dr. Harihara Iyer, Research Assistant
Edward Schmidlin, Electronics Engineer*

Graduate Research Assistants**

J. R. Brand (Resigned 7-17-67)
R. L. Brodzinski
T. J. Grant
K. W. MacMurdo
D. L. Uhl

Bert Long, Technician, part-time
Larry G. Eckstein, Technician, part-time
Mrs. Dorothy Pershing, Secretary, part-time

*Part-time

**Half-time or greater

IV. Publications and Talks

Publications

1. "Excitation Functions for the Helium Ion Induced Fission of Rhenium, Lutetium and Thulium", Phys. Rev., 153, 1270(1967). G. M. Raisbeck and J. W. Cobble.
2. "The Intermediate Energy Fission of Rhenium", Phys. Rev., 153, 1294(1967). C. Mannings and J. W. Cobble.
3. "The Thermodynamic Functions of Np(V) and Np(VI)", J. R. Brand and J. W. Cobble, Report No. COO-1716-1, submitted for publication.
4. "The Heat of Solution of Plutonium Metal and the Entropy of Pu(III)", R. J. Hinchey and J. W. Cobble, Report No. COO-347-27, submitted for publication.

Talks by the Staff

- 1) "The Solubility and Heat of Solution of Neptunyl Nitrate Hexahydrate and the Entropy of the Neptunyl Ion" by J. W. Cobble, 153rd. American Chemical Society Meeting, Miami, Florida, April 10, 1967.
- 2) "Fission Studies on Iridium", R. L. Brodzinski, Nuclear Chemistry Seminar, Purdue University, December 11, 1967.
- 3) "The Use of Senior Research in Teaching Nuclear Chemistry Techniques", J. W. Cobble, Nuclear Education Conference, NRC-NAS, Washington, D. C., November 13, 1967.
- 4) "Ternary Fission", R. E. Iyer, Nuclear Chemistry Seminar, Purdue University, October 9, 1967.