Thermodynamic Studies on Heavy Elements and
Studies in Nuclear Chemistry

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I. Introduction

This report summarizes the research activities carried out under contract AT(11-1)-1716 from January 1, 1972 to December 31, 1972. Research has been completed on the ternary fission of Pu^{239} induced by medium energy helium ions. Work continues on a number of heavy ion ternary fission studies, using C^{12} and Ne^{20} ions on gold and uranium. Feasibility studies have been made on producing neutron deficient americium isotopes from heavy ion bombardments, and studying their decay schemes, particularly spontaneous fission.

The thermodynamic functions of Eu^{+2} have been determined calorimetrically and a better value of the $\text{Eu}^{+2}/\text{Eu}^{+3}$ couple has been obtained.

During this period one graduate student has obtained his Ph.D. degree.

Some of the research given in this report is of a preliminary nature and should not be referred to without permission of the project director.

II. Research Activities

A. Nuclear Chemistry Research

1. The Binary and Ternary Fission of Pu^{239} Induced by Intermediate Energy Alpha Particles (McDaniel)

This project has been completed and the work submitted to the Physical Review for publication. The Abstract is as follows:

Cross section data for 59 nuclides formed in the fission of Pu^{239} induced by 42.4 MeV alpha particles have been obtained. A technique using recoil data was used to study the fission mass distribution products for $24 \leq A \leq 160$. The cross sections range over eight orders of magnitude. The data in the region $24 \leq A \leq 47$ were used to extend the study of ternary fission into a heavier system than previously studied in any detail radiochemically. A dramatic increase in some of the ternary fission yields correlates with an increased Z^2/A . An unsuspected shift of the ternary-binary transition point to lower A was also observed. A technique of high resolution gamma-ray spectroscopy was used for analysis of mixed fission product samples and separated nuclides. The total binary fission cross section for 42.4 MeV alpha particles on Pu^{239} was found to be 1490 ± 150 millibarns.

2. Binary and Ternary Fission of U^{238} Induced by Ne Ions (Otto)

The binary and ternary fission mass yield distribution resulting from the bombardment of natural uranium (99.27% U^{238}) excited to 70 MeV⁽¹⁾ by $\text{Ne}^{20}(8)$ ions is being studied radiochemically.

The use of heavy ions introduces three complications not encountered with lighter projectiles such as He^3 and He^4 when using catcher foil technique:

- 1) The center of mass has a significant forward velocity component.

2) The compound nucleus is known to have a large average angular momentum resulting in a forward backward anisotropy of the fission fragment distribution. 3) There is an increase in the possibilities for production of light radioisotopes such as Mg^{28} and Na^{24} by spallation reactions. It is clear then that the distribution of any radionuclide's activity in the target and recoil catcher foils depends on the importance of each of the above three factors. In the past the ratio of the forward catcher foil activity to backward catcher foil activity for a given radionuclide has been close to unity, and indicated that the activities resulted from fission and not from spallation.

This simplifying assumption is not valid with heavy ions. A catcher foil technique has been developed that will allow determination of the kinetic energy (k_{ff}), anisotropy $f(\theta)$, the average ratio of the velocity of the center of mass to the center of mass velocity of the fission fragment, ($v = \frac{V}{V_{cm}}$), the absolute cross section of the fission product, and the spallation contribution to the isotope activity. Two separate targets' geometries are used. One has the target and catcher foils 90° to the beam, and the second has the target and catcher foils 10° to the beam. The activity in the backward catcher and in the target plus forward catcher foil is determined for each geometry. The range energy relationship of the fission fragment in the uranium target foil and its thickness must also be known.

The values of kE_{ff} , $f(\theta)$, and σ are related to the fractional catcher activities using a simple vector model and classical energy and momentum conservation considerations.

An attempt was made to determine the absolute cross sections of several isotopes of elements from the first transition series by gamma-ray

spectroscopy. Estimated count rates for the chain yield were determined using the gaussian charge and mass distribution parameters provided by Karanyan, et al. (2,3). Ni, Mn and Co carriers were separated with various concentrations of HCl using a Dowex 1 x 8 50-100 mesh anion exchange column. The carriers were precipitated and counted using a Ge(Li) detector. The spectrum ranged from 30 keV to ~1400 keV. The results indicate that better separation of purification of the elements is required to decrease the compton background.

There was some indication that the Mn^{56} 846.7 keV line was seen.

The high yield binary products can be determined by gamma ray spectroscopy of a sample containing the gross fission products (4). This method along with gamma-ray spectroscopy of the rare earths separated with La^{+3} carrier is being employed.

The fission cross section for Ni^{66} and La^{140} and Pm^{148} have been determined. The equal charge displacement (ECD) rule and the gaussian charge distribution parameters given by Karanyan for $Ne^{20}(U^{238}, f)$ (3,4) were used to obtain the chain yield for $A=66$ and $A=140$. Using the $A=140$ point as a reference the $A=66$ cross section falls exactly on the predicted gaussian mass yield.

Several attempts have been made to determine Mg^{28} ternary cross section. The results indicate that a spallation reaction or reactions are contributing to Mg^{28} activity, possibly from a $Ne^{20}(O^{16}, \alpha, 4p)$ or a similar reaction. Removal of adsorbed surface oxygen from the silver catcher foil will be required.

The mass and charge distribution of the high yield $80 < A < 180$ binary fission products from Ne^{20} on U^{238} has been studied extensively by

Karanyan. (3,4)

The binary and ternary fission yields will be investigated for $20 \leq A \leq 225$. It will be necessary to determine the high yield binary mass and charge distribution to show a smooth continuation of the binary mass distribution into the region of $A \approx 40$. This will demonstrate the existence or non-existence of a separate ternary mass distribution.

The kinetic energy, anisotropy, and average center of mass velocity of several light binary and ternary fission products will be investigated using the techniques developed if large spallation interference can be eliminated.

The binary yield will continue to be investigated by high resolution gamma-ray spectroscopy.

Very heavy low yield fission products ($A > 200$) will be investigated by α -spectroscopy.

Work is also being done to improve existing chemical procedures. A complete ion exchange chemistry is being developed that will separate and purify carriers of Mg, Ca, Sr, Na, K, La, Mn, Fe, Co, Ni, Cu, Zn, or any combination of these elements. Short separation lines and high purity are the major requirements. The plate theory of ion exchange chromatography is being used to optimize both factors.

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3. Search for Ternary Fission in Gold Excited by Carbon Ions (Kasner).

The ternary fission of Au^{197} induced by C^{12} ions has been studied by determining the cross section for the formation of Mg^{28} . Foil Au^{197} targets (99.999% purity, 9.0-10.0 mg/cm^2 thick) were placed between two silver catcher foils (99.9999% purity) and irradiated for approximately 24 hours with C^{12} ions. All irradiations were carried out at the Yale University Heavy Ion Accelerator. The target package was then returned to Purdue University and each foil was radiochemically analyzed for Mg^{28} . The decay of the Mg^{28} was followed for several half-lives in a low-background beta counter. Regressive least-squares analysis of the resulting decay curve allowed accurate determination of the radiochemical yield and purity. To vary the incident beam energy silver foils were used as energy degraders ahead of the target package.

It was found that as the C^{12} beam passed through the several silver catcher foils a reaction was induced which had Mg^{28} as a product. Attempts to determine exactly what this reaction was were unsuccessful. It was, therefore, necessary to determine a " Mg^{28} blank" excitation function. A series of silver foils, arranged in a stack, was irradiated with C^{12} ion and the cross section for the formation of Mg^{28} was determined as a function of bombarding energy from -80-120 MeV. (Table 1).

Table 1.

Cross Sections for the Formation of Mg^{28} in Silver

Energy (MeV)	Cross Section (microbarns)	Energy (MeV)	Cross Section (microbarns)
120.9 ± 3.9	1.17 ± 0.15	103.3 ± 4.6	0.383 ± 0.030
120.7 ± 4.2	1.01 ± 0.10	93.7 ± 5.0	0.173 ± 0.041
112.2 ± 4.3	0.529 ± 0.064	83.4 ± 5.4	0.041 ± 0.010
112.1 ± 4.5	0.688 ± 0.099	59.5 ± 6.8	<0.002
104.4 ± 4.5	0.410 ± 0.048		

The excitation function shows a general trend of increasing cross section with increasing bombarding energy (Figure 1). Since the silver foils used to determine the excitation function were essentially identical to those used as catcher foils a blank correction factor could be calculated.

Because of the possibility of some unknown reaction in the gold foil which might have Mg^{28} as a product, there was no way to determine how much of the Mg^{28} found in the target was produced by ternary fission. Further, if some of this spallation Mg^{28} recoiled out of the target, the blank correction calculated might be incorrect. Therefore, it was necessary to use only the backward (180° to the beam) catcher foil, which could not contain any spallation products from gold, to calculate the total Mg^{28} cross section. Calculations based on the forward momentum of the compound nucleus, an estimated fission anisotropy, the range and kinetic energy of the Mg^{28} fission product show that 22-24% of the total Mg^{28} produced in fission will recoil into the backward catcher. This information, along with the blank correction, allowed calculation of the cross section for the formation of

Mg^{28} as a product of the C^{12} induced ternary fission of Au^{197} (Table 2).

Table 2.

Cross Sections for the Formation of Mg^{28} as a Fission Product

Bombarding Energy (MeV)	Excitation Energy (MeV)	Corrected Cross Section (microbarns) ⁽¹⁾	Mg^{28} Cross Section (microbarns)
114.2	89.4	$0.115 \pm .044$	$0.42 \pm .2$
112.3	87.6	0.151 ± 0.050	$0.55 \pm .2$
110.5	85.9	0.172 ± 0.035	$0.60 \pm .1$
105.3	81.0	0.089 ± 0.20	$0.32 \pm .1$
94.8	71.1	(2)	
84.7	61.6	(2)	

(1) The partial cross-section based on the backward catcher.

(2) The blank correction was greater than the uncorrected value.

Figure 2 shows the general shape of the excitation function and how it compares to the total binary fission excitation function as determined by Gordon et al. ⁽¹⁾

One of the characteristics of compound nuclei formed by heavy ions is their high angular momenta. It has been established that high angular momentum leads to an increase in binary fission probability. ^(2,3) By using heavy ions (such as C^{12} , O^{16} , and Ne^{20}) and light ions (such as He^4) to produce the same or similar compound nuclei, the effects of angular momentum on ternary fission might be established.

The ternary fission of the $\text{Pu}^{239} + \text{He}^4 + \text{Cm}^{243} + f$ system has been studied at moderate excitation energy (~40 MeV). ⁽⁴⁾ The similar compound

Figure 1. Excitation Function for Mg^{28} production in
Silver Catcher Foil.

Figure 2. Excitation Function for Fission Mg^{28} from Gold.

nucleus Cm^{244} can be made by $\text{C}^{12} + \text{Th}^{232}$. However, at 40 MeV of excitation energy, the compound nucleus formed by the heavy ion actually has a lower angular momentum than the compound nucleus formed by the light ion.*

The binary and ternary fission of the $\text{U}^{238} + \text{He}^4 \rightarrow \text{Pu}^{242} + f$ system have been well studied for a range of excitation energies from 20-115 MeV.^(5,6) The Z^2/A value for this compound nucleus is the same as for Ac^{217} (36.5) which can be formed by $\text{He}^{20} + \text{Au}^{197}$. Since $(Z^2/A)/50.13$ is the fissionability parameter, two nuclei that have the same Z^2/A , should have similar fission characteristics. Thus, even though these two compound nuclei are not the same, there is much about the effects of angular momentum on ternary fission that can be learned by the comparison of the fission characteristics of Ac^{217} and Pu^{242} .

Because a distribution of states is formed in compound nuclear reaction, no exact angular momentum value for a compound nucleus can be calculated. However, there are methods of calculating the average or most probable value of l for a compound nucleus. T. D. Thomas⁽⁷⁾ uses a simple model based on a square-well nuclear potential to calculate average angular momentum states and cross sections for compound nucleus formation. A classical model shows quite good agreement with these values (Figure 3) and was used to calculate the average angular momentum values for three systems (Figure 4).

* as calculated from the classical approximation

$$\bar{l} = \left\{ \frac{\mu}{\hbar^2} (E_{\text{cm}} - B) R_0^2 (A_1^{1/3} + A_2^{1/3})^2 \right\}^{1/2} \quad \begin{array}{l} \mu = \text{reduced mass} \\ B = \text{barrier} \end{array}$$

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4. The Ternary Fission of Au^{197} Induced by Ne^{20} (Kasner)

The excitation function for the formation of Mg^{28} from the fission of Ac^{217} ($\text{Ne}^{20} + \text{Au}^{197}$) is being determined in a manner similar to that used for Ac^{209} ($\text{C}^{12} + \text{Au}^{197}$). To eliminate the need to determine a " Mg^{28} blank" excitation function a recoil collector foil, through which the beam will not pass, will be used (Figure 5). The target holder will allow the beam to be degraded to any desired energy and is designed so that anything that passes through the collimator cannot strike the recoil collector. Thus, the only nuclei collected will be products of compound nuclear reactions in the target.

A collection efficiency, function, based on the fission anisotropy, the forward momentum of the compound nucleus, the range and kinetic energy of the fission product and the geometry of the collector has been derived. Using this function, the efficiency of collection of Mg^{28} is $15.1 \pm 0.1\%$.

In addition to determining the Mg^{28} excitation function a partial mass

Figure 3 Comparison of Quantum-Mechanical and Classical
Angular Momentum Calculations.

Figure 4. Angular Momentum Calculations for Various Heavy Ion Reactions.

Figure 5. Diagram of Recoil Collector Target.

distribution of the ternary fission products and the lighter binary fission products will be determined. It is hoped that by comparing these data with the data of Iyer and Cobble on He^4 and U^{238} , (5,6) the effects, if any, of angular momentum on ternary fission might be determined.

5. Neutron Deficient Americium Isotopes (Rudy)

The availability of a high energy ${}^6\text{Li}$ beam at the Yale Heavy Ion Accelerator opens up the possibility of forming neutron deficient americium isotopes ${}^{233-236}\text{Am}$ via ${}^{233}\text{U}({}^6\text{Li}, x\text{n})$ reactions. Appreciable cross sections for ${}^{197}\text{Au}({}^6\text{Li}, 3\text{n})$ and ${}^{197}\text{Au}({}^6\text{Li}, 4\text{n})$ reactions have been reported by Anderson et al. (1) The corresponding reactions for production of americium isotopes would be attenuated by competition between fission and neutron emission at each step of de-excitation of americium compound nuclei. However, the lower number of neutrons needed to evaporate from the ${}^{239}\text{Am}$ compound nucleus make the proposed reactions promising routes of forming neutron deficient americium isotopes.

In this study radiochemical attempts will be made to isolate ${}^{235-236}\text{Am}$ from mixed fission products and other actinides and then to use primarily gamma spectroscopy (Ge(Li)) to determine the half lives and decay schemes of the new species. The nuclide ${}^{234}\text{Am}$ can be produced via ${}^{233}\text{U}({}^6\text{Li}, 5\text{n})$ reactions. This nucleus is hypothesized to decay by spontaneous fission with a 2.6 minute half life. (2) This long half life for spontaneous fission assigned to this species is long enough for removal of the target from the beam line and subsequent counting of the fission pulses with a surface barrier detector. By varying the bombarding energy and observing the yield of the isomer one could confirm the isotope assignment by comparison with

statistical model calculations.

^{234}Am is predicted to decay primarily by electron-capture. When odd-odd nuclei of this type decay they leave the daughter nuclei highly excited due to large hindrance factors to K-bands found at lower excitation energies in even-even nuclei. From comparison between electron capture and fission barrier systematics Skobelev⁽³⁾ has shown that ^{234}Pu daughters of ^{234}Am could have enough excitation energy to fission. Should the yield of delayed fissioning species be high enough one could measure the mass distribution of a neutron deficient fissioning nucleus (^{234}Pu) far from the line of beta stability using standard electronic techniques. Roughly this would correspond to the mass distribution resulting from fission of ^{233}Pu by low neutrons.

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B. Thermodynamic Studies

1. Thermodynamic Functions of $\text{Eu}^{+2}(\text{aq})$. (Morss)

Europium is the rare-earth element for which the divalent state was first observed; it has been many years since europous solutions and compounds were first characterized. Yet, despite continuing interest in the chemistry of europium, the thermodynamic properties of europium-containing species have only recently begun to be well understood. These thermodynamic

properties are especially important for two reasons: (1) significant advances are being made to interpret the thermodynamic and spectroscopic properties of rare earths in terms of electronic configurations and (2) the aqueous ions of europium, because of their relative freedom from complexation and hydrolysis, are uniquely suited to a Second-Law entropy calculation and comparison with ionic models.

Burnett⁽¹⁾ attempted the first standard-state measurements on the aqueous ions of europium. He interpreted these measurements in terms of the reactions

and

Under Burnett's experimental conditions, if his calorimeter solutions were indeed O_2 -saturated, then more than sufficient O_2 was present in all his runs for the reaction

We avoided the difficulties of preparing and reacting EuO by following Burnett's suggestion to measure the heat of solution of $\text{EuCl}_2(c)$. We have also avoided the ambiguities between reactions (2) and (3) by using bromine as an oxidant, which has only a single reduced species:

Lastly, we have made a new measurement of the oxidation potential of the $\text{Eu(II)}\text{-Eu(III)}$ aqueous couple. From the heat and free-energy measurements we have calculated the entropy of $\text{Eu}^{2+}(\text{aq})$. Combined with other recent thermochemical measurements, the above experiments yield $\Delta H_f^\circ(\text{Eu}^{2+}, \text{aq}) = -(527.8 \pm 5.4) \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{Eu}^{3+}, \text{aq}) = -(604.8 \pm 3.8) \text{ kJ mol}^{-1}$, and

$\Delta H_f^\circ(\text{EuCl}_2, c) = -(824.4 \pm 5.9) \text{ kJ mol}^{-1}$. The Eu(III,II) electrode potential has been measured in dilute chloride solutions, with the recommended result $-(0.35 \pm 0.03)\text{V}$. These data have been combined to yield $S^\circ(\text{Eu}^{2+}, \text{aq}) = -(10 \pm 12) \text{ J deg}^{-1} \text{ mol}^{-1}$. This aqueous entropy, derived entirely from experimental measurements, may be compared with $-10 \text{ J deg}^{-1} \text{ mol}^{-1}$ calculated from a semi-empirical model based only on the charge and size (0.117 nm for Eu^{2+}) of monatomic ions. Therefore, not only are all enthalpy data on europium compounds and aquo-ions mutually self-consistent, but also free energy and entropy data agree as well. From the free-energy values, an electrode-potential diagram for europium aquo-ions is

A perusal of the heats and free energies of formation of $\text{Eu}^{3+}(\text{aq})$ in comparison with those of neighboring trivalent lanthanides shows that $\text{Eu}^{3+}(\text{aq})$ is about 80 kJ mol^{-1} less stable than its neighbors with respect to the metallic elements. A systematic treatment of rare-earth metals has shown that the high stability of the divalent $\text{Eu}(c)$, and to a lesser extent the stability of the divalent $\text{Yb}(c)$, are primarily responsible for the unusually low heats of formation of their trivalent ions.⁽²⁾

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III. Personnel

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IV. Publications and Talks

Publications

1. "Enthalpy of Formation of Europium Dichloride and Thermodynamic Properties of the +2 and +3 Aqueous Ions of Europium". L. R. Moras and H. O. Haug, accepted for publication in Journal of Chemical Thermodynamics.
2. "The Binary and Ternary Fission of Pu^{239} Induced by Intermediate Energy Alpha Particles. T. L. McDaniel and J. W. Cobble, submitted to Physical Review.

Talks

1. "Heavy Ion Induced Fission", R. J. Otto, Nuclear Chemistry Seminar, Purdue University, April 20, 1972.
2. "Binary and Ternary Fission of Pu^{239} ", T. L. McDaniel, Nuclear Chemistry Seminar, Purdue University, October 2, 1972.
3. "Heavy Ion Emission from Light Nuclei", C. R. Rudy, Nuclear Chemistry Seminar, Purdue University, January 15, 1973.