MASTER

ANNUAL REPORT

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

for the period

February 1970 to January 1971

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

Department of Chemistry

Purdue University
Lafayette, Indiana

January 1971

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Thermodynamic Studies on Heavy Elements and
Studies in Nuclear Chemistry

Annual Report

COO-1716-11

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January 1, 1971

Edited by

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for the

U. S. Atomic Energy Commission

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I. Introduction

This report summarizes the research activities carried out under contract AT(11-1)-1716 from January 1, 1970 to December 31, 1970. Work has continued on the chemically bound neutron, and ternary fission studies have been completed and written up for the fission of Th^{232} , Au^{197} and Bi^{209} , with He^4 ions. In the case of Au^{197} , we have succeeded in measuring the formation cross section of a typical ternary product, Mg^{28} as low as 0.01 nanobarns (10^{-12} barns).

The thermodynamic behavior of a typical actinide ion, UO_2^{++} , has been determined over an extended range of temperature, 0-100° from $\bar{C}_p^0$ measurements. Finally, our recent determination of the entropies of the trivalent lanthanides and Pu^{+3} has made it possible for us to predict the entropies of other actinide ions, and indeed, any ion in the periodic table.

During this contract period two additional Ph.D. candidates received their Ph.D. degrees.

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. Chemically Bound Neutron (Grant)

Research was continued on the project of binding neutrons in a LiF crystal containing defect centers at 4°K . Experimental conditions and previous results have been reported in Phys. Rev. Letters, 23, 741 (1969). Since some other laboratories have not been able to repeat these experiments, another series of measurements were made.

The additional evidence that has been obtained shows that neutrons have been retained in a LiF crystal at 4°K for periods up to 40 seconds. A LiF crystal, containing defect centers from gamma irradiation, was neutron irradiated in liquid helium with an average flux of $7 \times 10^6 \text{ n/cm}^2 \text{ sec}$ for one minute. The crystal was counted on a LiI(Eu) detector 40 seconds later. A composite energy spectrum of 139 runs (Fig 1) shows a very clear peak in the neutron energy region (channels 70-80). When a 20 mil piece of Cd is placed between the crystal and the detector, a composite spectrum of 101 runs reveals a smooth β - γ tail (Fig 2). The difference spectrum is shown in figure 3. The LiF crystal irradiated at room temperature did not show any evidence of neutrons being emitted. A composite spectrum of 33 runs is shown in Fig 4.

A net of 1.04 neutron events per run was observed for the series shown in Fig 1. As repeated experiments were carried out on the same crystal delayed neutrons continued to be observed; however, the events per run decreased. Figure 5 shows this decrease plotted against total neutron exposure. Thus the neutron 'retention' ability of the LiF crystal appears to be destroyed by continued neutron exposure. Preliminary data also indicate that the neutron events observed is not directly linear with neutron flux. As fluxes of $10^7 \text{ n/cm}^2 \text{ sec}$ and higher were used the neutron

events decreased.

Other experiments had negative or inconclusive results. An attempt to observe delayed neutrons in a KBr crystal containing defect centers gave negative results. The results of studies on 99.9% Li^7F are, to date, inconclusive. A natural LiF crystal containing defect centers was obtained from Argonne National Laboratory. This crystal was used by Ringo et al. in their work with bound neutrons reported in Phys. Rev. Letters 23, 1475 (1969). A series of 25 runs gave no indication of thermal neutrons being emitted thus duplicating the results of Ringo for this particular crystal.

At present work is being done to discover the factor that determines the 'uniqueness' of neutron retention in some LiF crystals but not others and to increase this retention factor. An electronic counting system is now being employed that will discriminate β - λ pulses from neutron pulses. This makes it possible to count samples more quickly after neutron bombardment.

We have demonstrated the neutron retention effect to two groups of scientists from Argonne and Oak Ridge.

Figure 1. Spectrum obtained from counting LiF crystals neutron irradiated at 4°K . Neutrons give counts in channels 60-80. (101 runs)

Figure 2. Spectrum obtained from counting LiF crystals neutron irradiated at 4°K through a Cd foil. (101 runs).

Figure 3. . Difference neutron spectrum of data in Figures 1 and 2.

Shaded area corresponds to neutron calibration peak.

Figure 4. Spectrum obtained by counting LiF crystals irradiated with neutrons at room temperature. (33 runs)

Figure 5. Net neutrons observed per run in a LiF neutron irradiated at 4°K as a function of total neutron exposure.

2. Studies on Chemically Bound Neutrons (Hagenauer)

A number of studies have been carried out on gamma irradiated LiF crystals to determine the important variables in neutron-retention. Unfortunately most of these studies have not been very effective due to very low neutron yields in many of the crystals used in the research. Consequently it appeared that a more effective counting system would have to be developed that would discriminate against high energy gamma rays and true neutron events in the solid state $\text{Li}^6\text{I}(\text{Eu})$ detector being used.

The ionizing events produced by the interaction of γ -rays and neutrons with $\text{Li}^6\text{I}(\text{Eu})$ crystals have different decay rates. This is the basis of separating the two ionizing events that deposit an equal amount of energy in the detector crystal. The neutron with a lower ionization decay rate will have an integrated signal with a slightly slower rise time.

The detector signal was taken from the tenth dynode of a 8053 photomultiplier tube. When the pulse was amplified with a double delay line amplifier the pulse width of the output was about 50 n sec greater for a neutron than for a γ -ray with equal energy deposition. This time difference is utilized for the discrimination circuit as shown in figure 6.

Figure 6. Neutron and gamma ray counting discrimination circuit.

The best results were obtained by setting the discriminator level of the single channel analyzer (following the time to pulse height converter) so that 85% of the neutron pulses fell within the discriminator settings. At this setting 90% of all pulses due to γ -rays with the same energy deposition were eliminated.

Somewhat different, however, were obtained from another $^6\text{LiI}(\text{Eu})$ detector. With this detector very few high energy γ -rays could be discriminated without a large sacrifice of neutron counting efficiency. In this case, the detector crystal may have been slightly thinner than the 2 mm crystal used for the first detector since the intrinsic γ -ray efficiency was 50% lower with the same neutron efficiency. This suggests that crystal thickness is critical for good γ -ray discrimination. Another important factor for discrimination appeared to be the intrinsic "jitter" for the leading edge which was reflected in the leading edge timing. This is a characteristic of the crystal itself.

With counter I, a sufficient improvement has been made to allow us to obtain good neutron counting data with fewer runs, and we are repeating the studies on changing γ -irradiation times, neutron irradiation times and a study of the neutron retention half-life.

3. Studies on Chemically Bound Neutrons - Vacancy Centers in LiF (Otto)

The optical absorption spectrum of gamma irradiated LiF single crystals was determined. A reliable, reproducible differential method was devised for determining the absorption coefficient of the F center and the four other vacancy centers existing within the crystal structure. Relationships between F center concentration and total gamma ray dosage, and between absorption coefficients of each of the five observed

peaks and total gamma dosage were studied. Crystals with approximately 10^{19} F centers/cm³ were irradiated with fast neutrons and changes in the vacancy concentrations were sought.

The optical absorption spectrum of the crystal, obtained with a Cary 14 spectrophotometer, revealed five peaks in the region from 200 nm to 600 nm. The peaks were identified as F(245), R₁(320), R₂(375), M(445), and N(545) centers. F centers were produced with the use of a ⁶⁰Co source. F center concentration varied almost linearly with dosage in the region from 1×10^{19} to 2.5×10^{19} F centers/cm³. The rate of production in this region was approximately 4.9×10^{11} F centers/Rad/Cm³. The other four peaks were formed at the same rate but their total concentrations were lower. Fast neutron fluxes of 10^6 nvt and of one and two minute duration produced no noticeable effects on the concentrations of the five peaks.

4. The Fission of Th²³² Induced by Intermediate Energy He⁴ Ions (Roginski)

This work has been complete and submitted to the Physical Review for publication. The abstract of the paper is as follows:

"The cross sections for thirty-four nuclides covering the mass range 24 to 199 formed from the He⁴ ion induced fission of Th²³² at 20-41 MeV have been determined radiochemically. The resulting mass yield curve clearly indicates contribution from at least three different types of fission: the symmetric binary, asymmetric binary and asymmetric ternary modes. The identification of very light fragments and the low limits set on Au¹⁹⁹ confirms the existence of ternary fission seen previously in this laboratory in plutonium compound nuclei. Certain similarities and differences in this fissioning system to other heavier elements is discussed."

5. Ternary Fission in Au¹⁹⁷ (Uhl, McDaniel)

Some recent studies in this laboratory have been directed toward the investigation of the correlation between ternary fission cross sections and Z^2/A or the fissionability parameter, X . The yields of Mg²⁸ are assumed to be proportional to the total ternary process. An interesting relationship exists, as shown in figure 6.²

In the data shown in figure, no Mg²⁸ was observed radiochemically; therefore, only the upper limit is recorded. It was of interest to try to fix as accurately as possible the formation cross section of Mg²⁸ from studies on Au¹⁹⁷.

Consequently a search for Mg²⁸ activity is being conducted at higher excitation energies in gold. Preliminary results indicate that the magnesium cross section extrapolated to the excitation energy of the data of figure 1 (46 MeV), 20 nanobarns, is lower than indicated by the upper limits.

These findings are in agreement with the theory of Cohen and Swiatecki¹ which predicts a strongly reduced or nonexistent cross section for the ternary fission process when the fissionability parameter falls below 0.67. Au¹⁹⁷ + He⁴ gives a compound nucleus below this critical value. Consequently, the ternary process is strongly inhibited in this system.

Another result which may prove interesting upon further study is the surprising discovery of Ca⁴⁷ activity from a gold sample irradiated with 78 and 65 MeV alphas. This is the first observation of any Ca⁴⁷ activity in any fission studies carried out in this laboratory. Ca⁴⁷ lies on a portion of the mass yield curve which is near the intersection of the binary

¹S. Cohen and W. J. Swiatecki, *Ann. Physik*, 19, 67 (1962); 22, 406 (1963).

²D. L. Uhl, Ph. D. Thesis, Purdue University (1970).

cross
and ternary sections and is therefore not normally formed by either
the binary or ternary process. Additional studies are indicated to
see if an abrupt change in the shape of the mass yield curve occurs at
higher energies (60-80 MeV).

Figure 7. Variation of Mg^{28} formation cross-section with the fissionability parameter, X , at $E_{\text{c.m.}} = 45.6$ MeV.

6. Ternary Fission Studies on Pu^{239} (McDaniel)

Previous work in this laboratory first demonstrated radiochemically the phenomenon of ternary fission. At present, no conclusive evidence has been produced to demonstrate the complete shape of lower mass region of the mass yield curve. The primary reason for this is the fact that Na^{24} is the lightest mass nuclide that is amenable to study by radiochemical means. It is possible that a higher mass compound nucleus will shift the entire ternary mass yield curve

toward the heavier masses. A comparison of the mass yield curves of two elements with different masses should indicate this fact. If this were the case, then the $\text{Na}^{24}/\text{Mg}^{28}$ ratio might be significant in determining if an inflection point to the curve exists in the mass region 24-26.

Toward this end the ternary mass distribution of Pu^{239} is being studied. Pu^{239} target foils have been ordered and received from Oak Ridge. These foils are approximately $10\text{mg}/\text{cm}^2$ and are coated with $2\text{mg}/\text{cm}^2$ of 99.9999% pure silver for protection against the atmosphere. Preliminary studies have been conducted on a recoil technique for collecting most (98%) fission products which recoil out of the target foil in the backward direction while eliminating most spallation products which tend to interfere with the chemistry and fission yields. (See figure 2).

A method is also under study to collect gross gamma ray spectra from a portion of the solution formed by the dissolution of the catcher foil. These spectra should give information leading to cross sections for several nuclides which are formed with high yields in the fission process, without the necessity for chemical separation.

The work thus far has been directed toward designing and perfecting a target assembly compatible with the ideas above and the Argonne 60 inch cyclotron. Some preliminary work has been done toward analyzing gross gamma ray spectra of fission targets.

7. Heavy Ion Ternary Fission Studies (Kasner)

During the year investigations of heavy ion induced ternary fission were continued. The system currently being studied is $C^{12} + Au^{197}$. The Yale University Heavy Ion Accelerator is being used as a source of C^{12} ions. Target materials are transported from Yale University to Purdue University and analyzed for various fission products.

Preliminary experiments using backward recoil collection indicated very little Mg^{28} (the ternary fission monitor) and Sr^{89} (the binary fission monitor) were being collected. The collection efficiency of the target was found to be $<10\%$ based on the binary fission cross section data of Seaborg et. al.¹ Apparently the large forward momentum imparted to the compound nucleus by the carbon beam precludes accurate recoil studies in the backward direction, where no spallation products would be seen.

In subsequent experiments a stacked foil assembly was used consisting of a gold target foil (19-21 mgm/cm²) sandwiched between silver catcher foils (10-12 mgm/cm²). Foils were of 99.9999% purity. Separate experiments were carried out at various energies to measure any possible spallation Mg^{28} formed from impurities. The Mg^{28} was chemically separated from the foils using non-active carrier techniques and its decay was followed in a low background β counter for several half-lives. The

¹G. T. Seaborg, G. E. Gordon, A. E. Larsh, J. Sikkeland, Phys. Rev., 120, 4, 1341, (1960).

cross-sections and energies are $5.0 \pm 0.7 \times 10^{-31} \text{ cm}^2$ @ 125 MeV, $5.1 \pm 0.7 \times 10^{-31} \text{ cm}^2$ @ 117 MeV, and $7.0 \pm 1.0 \times 10^{-31} \text{ cm}^2$ @ 110 MeV. It was also observed that currents ≥ 25 micro amperes will damage the foil package. Experiments to determine the excitation function for the formation of Mg^{28} are now being carried out. The techniques are the same as described above except that the Sr^{89} cross section is also determined. To lower the beam energy silver degrader foils are used. To date experiments at 117 and 110 MeV have been partially completed. While the data from the experiment at 110 MeV is not yet completely analyzed, the 117 MeV data indicate an approximate cross section of $7.0 \times 10^{-31} \text{ cm}^2$. This value is only approximate because, as yet, no corrections for spallation Mg^{28} can be made. Further, if the excitation function for Mg^{28} has a steep slope in this energy region, thick target calculations are not applicable.

B. Thermodynamic Studies on Heavy Elements

1. Thermodynamic Properties of $\text{UO}_2^{2+}(\text{aq})$ (Morss)

Uranyl nitrate dehydrate has been prepared in high purity by recrystallizing the hexahydrate and dehydrating it over 95% H_2SO_4 over a period of several weeks to constant weight. The heat of solution has been measured at six temperatures between 6° and 94° . The heat capacity of the pure salt has also been measured at 25° using a new heat-capacity microcalorimeter: $C_p [\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}, \text{c}] = (66.5 \pm 1.0) \text{ cal deg}^{-1} \text{ mol}^{-1}$.

These measurements have been combined to yield $\bar{C}_{P,2}^\circ (\text{UO}_2(\text{NO}_3)_2, \text{aq}) = -15.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at 25°C . From this datum, and from other published thermodynamic properties of $\text{UO}_2^{2+}(\text{aq})$ and $\text{NO}_3^-(\text{aq})$, the partial molal heat capacity and entropy of $\text{UO}_2^{2+}(\text{aq})$ have been calculated between 25°

and 100° (Table 1). From these values, all of the thermodynamic properties of uranium (VI) solutions can be calculated up to 100°C. Further, good estimates can be made for other actinide (VI) species.

$\bar{C}_{P_2}^{\circ} (\text{UO}_2^{2+}, \text{aq}, 25^{\circ}) = 81.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ on the scale defined by Criss and Cobble (J. Amer. Chem. Soc., 86, 5390 (1964)). This value is about 25 cal deg⁻¹ mol⁻¹ more positive than would be predicted from the $\bar{C}_{P_2}^{\circ}$ vs. $\bar{S}^{\circ}$ correlation diagram for simple cations. Therefore, it appears that the correspondence parameters for oxygenated and other complex cations will require experimental measurement of $\bar{C}_{P_2}^{\circ}$ for other such species before regularities among these ions can be established.

The details of the measurements and calculation on uranyl nitrate dehydrate are being prepared as a manuscript for publication in Inorganic Chemistry.

2. A Semi-Empirical Equation for Entropies of Aqueous Monatomic Ions (Moras)

A paper with this title was presented at the 160th National ACS Meeting, Chicago, September 18, 1970. The experimentally-available entropies of 54 aqueous ions were correlated against the charges and ionic radii using several equations which have some theoretical foundation. Using recent experimental entropies for several highly-charged ions, particularly our own trivalent lanthanide and actinide ions and recent values of ionic radii, an equation was selected which yielded the best least-squares straight-line relationship between entropy of hydration and a function of charge and ionic radius. The function best suited was found to be essentially that predicted by the Born equation.

Table 1
Partial Molal Heat Capacity and Entropy of $\text{UO}_2(\text{NO}_3)_2(\text{aq})$

<u>Temp</u> <u>(°C)</u>	<u>$\bar{C}_{P_2}^\circ$</u>	<u>$\bar{S}_2^\circ$</u>
0	-70	53.3
10	-40	51.4
20	-22	50.3
30	-10	49.8
40	-6	49.6
50	-7	49.4
60	-9	49.2
70	-12	48.8
80	-16	48.5
90	-20	48.0
100	-25	47.4

The equation is :

$$\bar{S}^{\circ} = \frac{3}{2} R \ln (\text{at. wt.}) - 7.853 \left[\frac{(|Z| + 3.0)^2}{R_c + R_{\text{corr}}} \right] + 61.25 + R \ln p$$

$\bar{S}^{\circ}$ = partial molal entropy in cal deg⁻¹ mol⁻¹

R = gas constant = 1.987 cal deg⁻¹ mol⁻¹

Z = ionic charge (oxidation number)

R_c = crystal radius (ionic radius in oxide coord. no. 6, as defined R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, Part B, 25, 925 (1969), and 26, 1046 (1970).

R_{corr} = 1.2 Å for cations

= 0.4 Å for anions

p = multiplicity (usually 2J + 1)

Figure 8 is a plot of "corrected" experimental entropies vs. the best-fit function of Z and r.

This equation has been used to predict entropies of many other aqueous ions, including trivalent actinide species. In several cases, the unusually large discrepancy between predicted and experimental values indicates the advisability of further experimental measurements or finding an additional parameter which significantly affects aqueous entropies.

The details of the correlation procedure, the best-fit equation, and the predicted entropies are being prepared for submission to the *Journal of the American Chemical Society*.

Figure 8. Experimental entropies of aqueous ions fitted to $f(Z,r)$
(Solid line in the least-squares fit of all ions; dashed lines
are the least-squares fit through ions of each value of $|Z|$).

III. Personnel

Dr. James W. Cobble, Project Director

Dr. Richard Hagenauer, Research Associate

Dr. Lester Morss, Research Associate*

Edward Schmidlin, Electronics Engineer**

Graduate Research Assistants

T. J. Grant

M. L. Kasner

T. L. McDaniel

R. J. Otto

T. C. Roginski (Resigned, 2-17-70)

D. L. Uhl (Resigned, 1-21-70)

J. L. Schulze (Undergraduate research student)

Jerry W. Clark, Technician**

Howard J. Gobstein (Undergraduate research technician)**

Mrs. Dorothy Pershing, Secretary**

*N. S. F. Postdoctoral Fellow, 9/1/70.

**Part-time

IV. Publications and Talks

Publications

1. "The Thermodynamic Functions for $\text{Pu}^{+3}(\text{aq})$ and the Entropies for some Trivalent Actinide Ions", R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, 9, 922 (1970).
2. "Standard State Entropies for the Aqueous Trivalent Lanthanide and Yttrium Ions", R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, 9, 917 (1970).
3. "The Thermodynamic Functions of $\text{Np}(\text{V})$ and $\text{Np}(\text{VI})$ ", J. R. Brand and J. W. Cobble, *Inorg. Chem.*, 9, 912 (1970).
4. "The Fission of Th^{232} Induced by Intermediate Energy He^4 Ions", T. C. Roginski, M. E. Davis and J. W. Cobble, submitted to *Physical Review*.
5. "Search for Ternary Fission Induced in Au^{197} , Bi^{209} and Pu^{239} by Intermediate Energy Helium Ions", D. L. Uhl, T. L. McDaniel and J. W. Cobble, submitted to *Physical Review*.

Talks by the Staff

1. "Search for Ternary Fission in Au^{197} , Bi^{209} and Pu^{239} ", D. L. Uhl, Nuclear Chemistry Seminar, Purdue University, January 5 (1970).
2. "Correlation of Entropies of Inorganic Ions", L. R. Morsa, American Chemical Society National Meeting, Chicago, Illinois, September 24, 1970.
3. "Thermodynamics", by J. W. Cobble, Seminar at the University of Nevada, Reno, Nevada, November 19, 1970.