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ANNUAL REPORT

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

for the period

February 1969 to January 1970

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

Department of Chemistry

Purdue University
Lafayette, Indiana

January 1970

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Thermodynamic Studies on Heavy Elements and
Studies in Nuclear Chemistry

Annual Report

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U. S. Atomic Energy Commission

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I. Introduction

This report contains summaries and information on the research activities carried out under contract AT(11-1)-1716 from January 1, 1969 to December 31, 1969. During this period research has been carried out on the chemically bound neutron, and ternary fission in high and low Z elements. Further, a consistent set of entropies for the aqueous actinide and lanthanide trivalent ions has been determined. These revised thermodynamic functions will allow, for the first time, some important thermodynamic functions under standard state conditions to be fixed for these interesting species. During the contract period two additional Ph.D. candidates have completed their thesis research.

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)

During the spring of 1968 some preliminary experiments were carried out to see if there was any possibility of forming a weak, transitory bond between the magnetic moment of a neutron and a delocalized electron. Some of these preliminary experiments gave a few positive results, encouraging enough so that during the last two years some effort was put into the study. Eventually enough evidence was obtained that was consistent with weak "chemical" bonding, and the research was written up and published in Phys. Rev. Letters, 23, 741 (1969). The abstract of the paper is as follows:

Evidence has been obtained that neutrons form a weak bond with electrons trapped in LiF at 4°K . The chemistry of the resulting n^{-} species has been studied and shows that it decomposes at this temperature with a half-time in LiF of ~30 sec. The bond energy is probably about 0.1 eV. Removal of the trapped electrons greatly reduces, if not completely destroys, the neutron retention in LiF.

2. Additional Sources for Chemically Bound Neutrons (Hagenauer)

Following the discovery of "chemically bound neutrons" in gamma irradiated LiF, new possible types of neutron binding materials were tested including paramagnetic and high magnetic susceptibility ions, and other crystals with stable "F" centers. Targets were Na_2O_2 , FeCl_3 , Ho_2O_3 , TbO_2 , metallic Na, metallic Li, and "F" center crystals of KBr and NaCl. Negative results were obtained for all targets except Ho_2O_3 and NaCl whose results are still uncertain.

3. Ternary Fission of Thorium (Roginski)

A ternary fission mass yield curve of Th^{232} irradiated with 41 MeV He^4 has been determined. It was found that the ternary fission cross section increased exponentially from an upper limit of 1.2 nanobarns for Ca^{47} to a value of 730 nanobarns for Na^{24} . This trend was shown to be opposite from the trend of light binary fission products of Th^{232} . The cross section of light binary fission isotopes decreases rapidly from 170 microbarns for Zn^{72} to 29 microbarns for Ni^{66} to 565 nanobarns for Mn^{56} . The mass yield curve is shown in figure 1.

The ternary fission of Th^{232} irradiated with protons was also studied. Problems with spallation reactions on impurities prevented a detailed study of the ternary fission mass yield curve. After subtracting the estimated spallation-produced Mg^{28} , the cross section for Mg^{28} production from ternary fission is 68 nanobarns.

A comparison of the various ternary fission studies from this laboratory shows an interesting trend with the irradiating particle. Comparing the results obtained from H^1 , He^3 , and He^4 irradiations, the probability for ternary fission apparently increases with the mass of the bombarding particle faster than the total fission cross section. This trend would indicate a strong angular momentum effect.

4. Search for Ternary Fission in Au^{197} , Bi^{209} and Pu^{239} Induced with He^4 Ions (Uhl)

This research has been completed and will be submitted for publication in the Physical Review. A brief summary is as follows:

In order to study how widespread the ternary fission process is in

Figure 1. Mass-yield curve for the fission of Th^{232} with 41 MeV He^4 .

compound nuclei, a search for the fission derived Mg^{28} formed in the irradiation of widely varying target materials with He^4 ions has been carried out.

Mg^{28} and Ca^{47} were used as the ternary fission monitors (when the Mg^{28} cross section was greater than the Ca^{47} cross section). It is assumed that the Mg^{28} represents a true ternary fission event. Sr^{89} was used as the binary fission monitor. A value for Ni^{66} and an upper limit for S^{38} were also determined for Bi^{209} fission.

Impurity contributions to Mg^{28} activity via spallation reactions posed a particular problem. Cross sections for these reactions and the impurity levels for isotopes which could form Mg^{28} had to be known accurately for the bismuth and gold experiments. Plutonium values were obtained from backward recoils and only the impurity level in the silver catcher foils was of importance. No activity attributable to Ca^{47} and S^{38} was obtained and upper limits were set for these isotopes. Sr^{89} and Ni^{66} were of sufficient activity that possible impurity corrections were insignificant.

An excitation function (figure 2) has been obtained for Mg^{28} formed in the ternary fission of Bi^{209} . This clearly indicates the dependence of ternary fission on energy and has little resemblance to a spallation product excitation function. No evidence for ternary fission occurring up to and including an excitation energy of 45.6 MeV in Au^{197} could be found.

Figure 3 illustrates an interesting difference between the ternary fission of gold and heavier elements. The $\sigma_{\text{Mg}^{28}}/\sigma_{\text{binary}}$ ratio appears to be independent of energy in Bi^{209} while it changes rapidly with energy in U^{238} .

Figure 2. Excitation function for Mg^{28} formed in the ternary fission of Bi^{209} with He^4 ions.

Figure 3. Ratio of $\sigma_{\text{Mg}^{28}}$ to $\sigma_{\text{binary fission}}$ for Bi^{209}
irradiated with He^4 ions.

Figure 4 summarizes much of the data on ternary fission at intermediate energies obtained in this laboratory. The Mg^{28} cross sections for the various isotopes at an excitation energy of 45.6 MeV (upper curve) and 35.4 MeV (lower curve) are plotted as a function of Z^2/A and X , the fissionability parameter. The solid symbols are data from this laboratory (Iyer, Cobble, Roginski and this research). The open symbols are similar data which have been extrapolated to the appropriate energy. The Mg^{28} cross sections, and therefore the ternary fission cross sections, steadily increase above a value of $x = .67$. Below $x = .67$, the ternary fission cross section drops off very rapidly.

In 1962, Cohen and Swiatecki concluded that the saddle-point shapes changed near $x = .67$. The result of their calculations indicated that these shapes change from dumbbell-like (approximated by two tangent spheroids) for $x \leq .67$ to cylinder-like (approximated by two overlapping spheroids) for $x \geq .67$. This cylinder-like shape has the possibility of forming two necks and hence three bodies in the saddle-point shape which the dumbbell-like shape is less probable of forming.

5. Range of Mg^{28} from Ternary Fission of U^{238} with 35 MeV Protons (Hagenauer)

Preliminary range experiments were made of a ternary fission product Mg^{28} , from U^{238} irradiated with 35 MeV protons using stacked foils of aluminum catchers. A range of 16.8 mg/cm^2 was observed, a much higher value than that obtained from other experiments. At this time the experiment was terminated to work on a new project.

Figure 4. Variation of σ_{Mg}^{28} with Z^2/A

6. Heavy Ion Ternary Fission Studies (Kasner)

An investigation of the effects of angular momentum on ternary fission has been initiated. This investigation is to be carried out by forming nuclei of high angular momentum by bombardment with heavy ions. The fission of the compound nucleus formed by the bombardment of Au^{197} by C^{12} ions was chosen for the initial experiments since the binary fission of this compound nucleus has been well studied. The first experiment was performed in early August (8/1 to 8/12). A stacked foil target (9.5 mgm/cm² Au target foil between 14.3 mgm/cm² Ag catcher foils) was irradiated at U. C. Berkeley HILAC Facility with 100 MeV carbon ions. The target was returned to Purdue University and Mg^{28} was chemically separated. However, possibly due to spallation reactions, the cross-section for the production of Mg^{28} was several orders of magnitude greater than expected.

In order to eliminate collection of spallation products along with fission products, a different target design will be used in future experiments. In this new design, the heavy ion beam will not pass through the catcher foils and only the fission products scattered back in the direction towards the beam source will be collected. Thus there will be no reaction with the catcher foils and products of spallation reactions with impurities in the target foil will continue in the "forward" direction and not be collected. The catcher foil will be arranged in a cylinder surrounding the target foil and will collect all fission products recoiling within a critical angle. This angle depends upon the length of the catcher foil and the diameter of the cylinder. The first experiments with this type of target are scheduled for early this spring.

B. Chemical Thermodynamics

1. Thermodynamic Functions for $\text{Pu}^{+3}(\text{aq})$ (Hinchey)

This research has been completed and accepted for publication in the March, 1970 issue of Inorganic Chemistry. An abstract of the paper follows:

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⁻¹, respectively. The heat of solution of $\text{PuCl}_3 \cdot 6\text{H}_2\text{O} (\text{c})$ has been measured as -8.056 ± 0.032 Kcal mole⁻¹. This value, together with measurements of the solubility of $\text{PuCl}_3 \cdot 6\text{H}_2\text{O} (\text{c})$ and reasonable estimates of the activity and osmotic coefficients, leads to a value of -47.9 gbs mole⁻¹ for the entropy of $\text{Pu}^{+3}(\text{aq})$. A consistent set of entropies has been generated for some other actinide (III) ions.

2. Standard State Entropies for the Aqueous Trivalent Lanthanide Ions and Yttrium Ions (Hinchey)

This research was completed and accepted for publication in the March, 1970 issue of Inorganic Chemistry. An abstract of the paper follows:

The partial molal entropies of thirteen trivalent rare earth and yttrium ions at 25° have been calculated from data in the literature and from this research on the heats and free energies of solution of the hydrated trivalent chlorides. These entropies are from 10 to 15 gbs mole⁻¹ more negative than previous estimates based on the old experimental value for $\text{Gd}^{+3}(\text{aq})$. The entropies of the lanthanide ions correlate well with the ionic radius if the internal electronic entropy is first subtracted. Consequently the present data do not demonstrate any effects on the

entropy of the postulated change in hydration number occurring near the middle of the 4f group.

3. Partial Molal Heat Capacity of $\text{UO}_2^{++}(\text{aq})$ (Morss)

Considerable difficulty has been encountered over the last few years in attempting to obtain $\overline{C}_{P2}^{\circ}$ values for the $\text{UO}_2^{++}(\text{aq})$ ion. Such a function would be extremely useful in attempting to calculate and predict the thermodynamic properties of MO_2^{+} and MO_2^{++} ions at temperatures other than 25°C . Previous attempts have been based on measuring the heats-of-solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or UO_2Cl_2 between 25 - 100°C . Unfortunately UNH is not a very good calorimetric material over this temperature range because it will not remain at constant composition. UO_2Cl_2 has too high a heat of solution and it appears to introduce too much error in the derived values of $\overline{C}_{P2}^{\circ}$.

A better salt appears to be the uranyl nitrate di-hydrate, which once prepared, is stable to water loss over 25 - 100°C and has a modest heat of solution. Uranyl nitrate dihydrate has been prepared in high purity by two methods: (1) dehydrating the hexahydrate over H_2SO_4 to constant weight; (2) crystallizing the dihydrate directly from fuming HNO_3 . The heat capacity of the aqueous uranyl ion is now being determined by measuring the heat of solution of this salt between 0° and 100°C .

III. Personnel

Dr. James W. Cobble, Project Director

Dr. Richard Hagenauer, Research Associate

Dr. Richard Hinchey, Research Associate (Resigned 8-13-69)

Dr. Lester Morss, Research Associate

Edward Schmidlin, Electronics Engineer*

Graduate Research Assistants

T. J. Grant**

M. L. Kasner*

T. L. McDaniel*

T. C. Roginski**

D. L. Uhl**

Bert Long, Technician* (Resigned 5-2-69)

Jerry W. Clark, Technician*

Mrs. Dorothy Pershing, Secretary*

* Part-time

** Half-time or greater

IV. Publications and Talks

Publications

1. "Evidence for Discovery of Chemically Bound Neutrons", Phys. Rev. Letters, 23, 741 (1969). T. J. Grant and J. W. Cobble.
2. "Binary and Ternary Fission of U^{238} Induced by Intermediate Energy He^3 Ions", Phys. Rev., 182, 1303 (1969). K. W. MacMurdo and J. W. Cobble.
3. "The Thermodynamic Functions for $Pu^{+3}(aq)$ and the Entropies For Some Trivalent Actinide Ions", accepted for publication, Inorganic Chemistry, March (1970). R. J. Hinchey and J. W. Cobble.
4. "Standard State Entropies for the Aqueous Trivalent Lanthanide and Yttrium Ions", accepted for publication, Inorganic Chemistry, March (1970). R. J. Hinchey and J. W. Cobble.
5. "The Thermodynamic Functions of $Np(V)$ and $Np(VI)$ ", accepted for publication, Inorganic Chemistry, March (1970). J. R. Brand and J. W. Cobble.

Talks by the Staff

1. "Chemically Bound Neutrons", by J. W. Cobble, seminar at Purdue University, Department of Chemistry, September 25, 1969.
2. "Solution Thermodynamics", by J. W. Cobble, seminar at Whiteshell Nuclear Research Establishment, Pinawa, Canada, October 7, 1969.
3. "Solution Thermodynamics", by J. W. Cobble, seminar at University of Calgary, Department of Chemistry, Calgary, Canada, October 9, 1969.
4. "Ternary Fission of Th^{232} ", by T. C. Roginski, seminar at Purdue University, Department of Chemistry, October 27, 1969.
5. "Chemistry of Berkelium", by L. R. Morss, seminar at Purdue University, Department of Chemistry, December 18, 1969.

J. W. Cobble gave a series of nine talks at various local midwestern ACS Sections in the spring of 1969 on "Chemical Thermodynamics".