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THERMODYNAMICS OF THE ACTINIDES

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THERMODYNAMICS OF THE ACTINIDES

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INTRODUCTION

Herein, the term "actinides" is applied to the elements of atomic number 89-103. All members of the series have now been discovered^[1] but the production of weighable amounts of the elements has not been extended beyond einsteinium (atomic number 99). There is little hope that experiments with macroscopic quantities of the transeinsteinium elements ever will be possible, owing to the very short half lives of even their most stable isotopes. It has been of particular interest, therefore, to attempt to discover whether the properties of the more stable elements of this series vary in a sufficiently systematic way to justify confidence in the prediction of the properties of macroscopic amounts of the heavier elements. In this connection, at the Lawrence Radiation Laboratory in Berkeley, particular effort has been devoted to the investigation of the transplutonium elements.

Electronic Configurations

Optical and atomic beam resonance methods have been used to determine the electronic configurations^[2,3] of the neutral gaseous atoms of the actinides through curium, with the results shown in Table I. On the basis of their electronic configuration the transactinium elements, with the exception of thorium, are members of a 5f transition series. The gaseous ion Th^{+3} (spectroscopic notation, Th IV) has been shown to have a $5f^1$ configuration,^[2] and Th^{+3} may therefore be included in the series. The lighter actinides are more readily oxidized beyond the +3 state than are the 4f (lanthanide) elements, doubtless because the lighter 5f elements have smaller values for their fourth,

TABLE I

Electronic Configurations of the Actinides

Radon core plus $7s^2$ plus:

Element	Ac	Th	Pa	U	Np	Pu	Am	Cm
Configuration	6d	6d ²	5f ² 6d	5f ³ 6d	5f ⁴ 6d	5f ⁶	5f ⁷	5f ⁷ 6d

fifth and sixth ionization potentials. [3]

Properties of Metals

A. Americium

Americium metal was first prepared by Westrum and Eyring [4] who noted that it was less dense (bulk density $11.7 \pm 0.3 \text{ gm cm}^{-3}$) and more malleable and ductile than plutonium. Westrum and Eyring, [4] as well as Lohr and Cunningham, [5] measured the heat of solution of the metal in 1.5 M HCl, and found a value of $162 \pm 3 \text{ Kcal mol}^{-1}$.

The first investigation of the crystal structure of americium metal revealed the existence of an alpha lanthanum-like double hexagonal close packed phase (space group $P6_3/mmc$) with lattice parameters:

$$a_o = 3.642 \pm 0.005A, \quad c_o = 11.76 \pm 0.01A$$

at room temperature, with a calculated density of $11.87 \pm 0.05 \text{ gm}$. [6]

A second double hexagonal close packed phase, having lattice parameters:

$$a_o = 3.474 \pm 0.005A, \quad \text{and} \quad c_o = 11.25A,$$

as well as a face centered cubic phase (obtained by condensation of americium metal vapor on tantalum) with $a = 4.895 \pm 0.005A$,

have been reported by McWhan, Wallmann, Cunningham, Asprey, Ellinger and Zachariasen. [7] Both of these phases have calculated densities of 13.7, and a metallic radius ($C. N. 12$) = 1.73A.

The thermodynamics relationship among these phases is not clear at the present time. In an attempt to establish the temperature order of stability McWhan, Cunningham and Wallmann [8] investigated the crystal structure of the more dense double hexagonal phase of the metal from -120 to +605°C. No change in the structure or discontinuity in the expansion behavior was observed in this temperature interval. Because

of rapid volatilization of americium and reaction with the quartz x-ray capillaries, the extension of the investigation to higher temperatures was not feasible at the exposure times required for the standard x-ray equipment. Exposure times were shortened, however, by wrapping the protected film directly around the high temperature oven (~3 cm diameter). By this means diffraction patterns were obtained at 700 and 850°C. Although extensive volatilization of the metal and oxidation to AmO still occurred during the exposure, a few lines were obtained which could be indexed as fcc with $a = 4.91\text{\AA}$. This cell constant is consistent with the room temperature value for the fcc phase and its experimentally determined thermal coefficient of expansion. (See below.)

Coefficients of thermal expansion were calculated for both the fcc and double hexagonal close packed phases, the former from diffraction patterns taken on a single sample at about 50° intervals from 22 to 360°C, and the latter on two samples of metal, the first from 20 to 605°C, and the second from -121 to 588°C.

The data were then fitted to a polynomial of second order by the method of least squares, with the results:

Sample No. 1.

$$a_T = 3.4671 + 2.62 \times 10^{-5}T + 0.56 \times 10^{-8}T^2$$

$$c_T = 11.238 + 6.59 \times 10^{-5}T + 6.3 \times 10^{-8}T^2$$

Sample No. 2.

$$a_T = 3.4673 + 2.57 \times 10^{-5}T + 0.52 \times 10^{-8}T^2$$

$$c_T = 11.236 + 7.31 \times 10^{-5}T + 7.3 \times 10^{-8}T^2$$

As mentioned previously, in contrast to the behavior of plutonium, no anomalies were noted in the expansion behavior of americium.

Melting Point of Americium.

A number of early attempts to determine the melting point of americium failed to yield satisfactory values, owing, no doubt to the formation of a hard oxide skin on the surface of the small samples of metal. McWhan, Cunningham and Wallmann^[8] overcame this difficulty by "soldering" fine tantalum wires together with freshly produced americium metal, and subjecting the join to a mild strain at gradually increasing temperatures until parting occurred.

The method was first investigated with similar quantities of pure rare earth metals of known melting point and found to be reliable to about $\pm 5^{\circ}\text{C}$. The best values for the melting point of americium, as determined by this method, is $995 \pm 7^{\circ}\text{C}$.

Magnetic Susceptibility of Americium.

McWhan and Cunningham^[9] have investigated the susceptibility of several samples of americium metal in the temperature range from -196 to 550°C . Accurate measurements are difficult because of the low susceptibility of the metal, but from these measurements the temperature variations of the susceptibility may be set at less than 7% in the interval studied. The value for the susceptibility at room temperature is:

$$\chi_{20^{\circ}\text{C}} = (881 \pm 46) \times 10^{-6} \text{ erg gauss}^{-2} \text{ mol}^{-1}$$

There have been several measurements of the susceptibility of Am^{+3} , both in aqueous solution and in compounds. The data are in poor agreement, especially as regards the magnitude of the temperature dependence. Howland and Calvin^[10] found χ_M for Am^{+3} ion in dilute acid solution to be $720 \times 10^{-6} \text{ ergs gauss}^{-2} \text{ mol}^{-1}$ at room temperature. Crane, Wallmann and Cunningham^[11] found a much higher

value (namely, 1040) for AmF_3 at 295°K and a marked temperature dependence (1740 at 77°K). Recent measurements [9] on Am^{+3} adsorbed on a single bead of cation exchange resin ("Dowex 50") give a value of 670 ± 100 at 20°C and 744 ± 120 at 77°K . The room temperature value agrees with that of Howland and Calvin within experimental error. The higher susceptibility and more pronounced temperature dependence observed by Crane, et al, for americium trifluoride may have been due to the presence of a small amount of curium impurity in their sample ($\chi_{\text{M}_{20}^\circ} \text{Cm}^{+3} = 24,000$ cgs units).

The susceptibility of americium metal appears to be slightly higher than that of the $+3$ ion and the temperature dependence to be slightly less. These differences, however, are barely outside the present rather large experimental errors.

An analysis by Gruber [12] of the low lying electronic levels of Am^{+3} in a lanthanum trichloride matrix gives a separation of 2215 cm^{-1} between the ground state, $^7\text{F}_0$, and the next higher $J = 1$ level. The separation is such that the higher level is only slightly populated, even at temperatures as high as 850°K ($\sim 600 \text{ cm}^{-1}$).

The susceptibility of Am^{+3} arises, then, almost entirely from temperature independent second order terms of the ground level, in agreement with those measurements which show but little temperature dependence.

Although both Am^{+3} and Eu^{+3} have an f^6 configuration for the ground state, the calculation of a theoretical value for the susceptibility of Am^{+3} is more difficult than for Eu^{+3} , since the departure from pure LS coupling is quite significant for americium.

Gruber [12] has made a preliminary calculation of the mixing of

the 5D_0 and 3P_0 levels with the ground state of Am^{+3} . From his results McWhan and Cunningham [9] calculate a value of 682×10^{-6} ergs gauss⁻² for the molar susceptibility of the ion. The agreement with the experimental values is considered reasonably satisfactory.

The susceptibility data strongly suggest that there are close to three electrons per atom in the conduction band in the metal, in disagreement with the valence assignment proposed by Zachariasen. [13]

B. Curium

Wallmann, Cunningham and Fuger [14] have obtained data on the crystal structure, melting point and heat of solution of curium metal in 1 M HCl. Marei and Cunningham [15] have measured the magnetic susceptibility from 77 to 350° K.

A mixture of face centered cubic and hexagonal phases is obtained by reduction of the trifluoride with barium vapor at ~ 1300° C.

Preliminary values for the lattice parameters of the hexagonal phase are:

$$a_0 = 3.50 \text{ \AA}$$

$$c_0 = 11.3 \text{ \AA}$$

The unit cell volume is about three percent more than that of the more dense hexagonal phase of americium.

The melting point is $1340 \pm 40^\circ \text{ C}$.

The susceptibility data are given in Table II.

Within the accuracy of measurements, the metal obeys the Curie-Weiss relationship down to liquid nitrogen temperatures. The molar susceptibility of the metal is similar to that of the trifluoride as measured by Crane, Wallmann and Cunningham. [11]

TABLE II

Magnetic Susceptibility of
Curium Metal

T ($^{\circ}$ K)	χ_m (c g s units) $\times 10^6$
329	$16,700 \pm 400$
306	$17,600 \pm 400$
297	$17,700 \pm 400$
273	$18,400 \pm 400$
230	$20,100 \pm 400$
77	$32,200 \pm 400$

The heat of solution of curium metal in 1 M HCl is -138 ± 7 Kcal mol⁻¹, similar to that of plutonium, but some 20 kilocalories more positive than that of americium. The more electropositive nature of americium may be associated with its low heat of vaporization,^[15]

SUMMARY OF PROPERTIES OF THE METALS

In the metallic state, the next two elements beyond plutonium are rare-earth-like in character in conformity with their general rare earth-like chemical behavior. As shown by tracer experiments on the actinide elements through mendelevium the +3 state persists with high stability throughout the rest of the series. It appears probable that the metals beyond curium will, in general, resemble the rare earth elements in structure and properties.

Zachariasen^[13] has calculated values for the numbers of valence and 5f electrons in the actinide metals, on the basis of observed inter-atomic distances in the solid phases. He assigns 5.5 f electrons and 3.5 valence electrons to the face centered cubic and more dense double hexagonal close packed phases of americium. Our lattice parameters for metallic curium, a predominantly trivalent element, suggests that the number of valence electrons in both curium and the more dense form of americium is close to three.

II. Properties of Actinide Crystals

CRYSTAL FIELD SPLITTING IN THE ACTINIDE TRICHLORIDES

Crystal field stabilization plays an important part in determining the thermodynamic stability of "d" transition element compounds and it has been of interest, therefore, to determine crystal field splittings for some compounds of the actinide elements. Lammermann and Stapleton^[16] have examined the optical and paramagnetic resonance

spectrum of tripositive plutonium in both a lanthanum trichloride and a lanthanum ethyl sulfate matrix and find that the crystal field splitting of the levels is small and of about the same magnitude as observed in the analagous lanthanide ion, Sm^{+3} . Gruber^[12] has observed crystal field splittings for Am^{+3} in a LaCl_3 matrix to be similar to those found for Eu^{+3} . For the trivalent actinides, crystal field effects appear to have little more importance in determining the stability of various compounds than in the case of the lanthanides.

CRYSTAL STRUCTURES OF THE TRICHLORIDES OF CURIUM AND CALIFORNIUM

The trichlorides of the lanthanide elements exhibit the hexagonal UCl_3 structure type from lanthanum through gadolinium, a triclinic structure from holmium to lutecium, while TbCl_3 and DyCl_3 have a structure which has not yet been identified. It seems reasonable to suppose that the transition from one structure type to another is determined primarily by the ratio of the radius of the metal cation to that of the chloride ion. For a given number of electrons in the f subshell the trivalent actinide ions are 0.02 to 0.03A larger than the corresponding trivalent rare earths. Hence, if radius ratio is the critical factor, the UCl_3 structure might be expected to persist in the actinide trichlorides to about element 99 (einsteinium).

Wallmann and Cunningham^[17] have obtained the diffraction patterns of CmCl_3 and CfCl_3 and find that both have the hexagonal structure, as expected.

III. Magnetic Properties of the Actinide Compounds

As have been mentioned previously, analyses of the optical absorption spectra of the trivalent actinides in a LaCl_3 matrix by Gruber,^[12] and by Lammermann and Stapleton^[16] have shown that the

departure from pure LS coupling in the ground state is considerably greater for the heavier f transition elements than for the lanthanides. The analysis of the spectrum of Pu^{+3} in LaCl_3 by Lammermann and Stapleton is sufficiently extensive to allow a good comparison to be made between calculated magnetic susceptibilities for PuCl_3 and the experimental values reported by Dawson, Mandelberg and Davies. [18]

The comparison [9] is shown in Table III.

The susceptibility minimum indicated by the experimental point at 548°K is not predicted by the theoretical calculations, and perhaps should be reinvestigated. The magnetic susceptibilities of Bk^{+3} and Cf^{+3} (adsorbed on the cation exchange resin Dowex 50) have been measured from 77°K to somewhat above room temperature, but analyses of the spectra of the ions are not sufficiently detailed as yet to permit an accurate comparison of experimental and theoretical values.

Cunningham, Wallmann, Phillips and Gatti [19] have attempted to measure the magnetic susceptibility of the tripositive ion of einsteinium, using approximately $0.003 \mu\text{g}$ of the oxide.

Complications arise in measuring the susceptibilities of highly radioactive samples because of paramagnetism induced in the supporting matrix by the radioactive disintegration of the sample. The principal isotope used for the susceptibility measurements on einsteinium was the 20 day α -emitting E^{253} .

In order to correct for the induced paramagnetism, the susceptibility of the sample was measured as a function of time, and extrapolated to zero time. The data thus corrected gives μ_{eff} for

TABLE III

Magnetic Susceptibility of PuCl_3

Temp	Experimental $\chi_m (\times 10^6)$	Theoretical
90°K	1607	1567
200	887	829
300	658	628
334	606	587
373	571	549
397	548	529
428	525	507
457	515	490
491	484	472
520	464	458
548	462	447
583	472	434
300°	659	

$$E^{+3} = 8.1 \pm 1.5 \text{ Bohr magnetons.}$$

CONCLUSIONS

On the basis of present knowledge of the properties of the actinide elements, it would appear probable that the thermodynamic properties of the transcurium elements probably will be rather similar to those of curium with a more or less regular variation as a function of atomic number, as observed in the lanthanide elements.

The remaining elements in the series will be predominantly tri-positive, and their crystallography will resemble that of the corresponding rare earth element of similar ionic radius.

Magnetic and optical properties will resemble those of the analogous lanthanide elements, after making allowance for the greater multiplet splitting and more significant departure from LS coupling for the heavier elements.

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