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SHIFTED HOMOLOGOUS RELATIONSHIPS BETWEEN THE TRANSPLUTONIUM AND EARLY RARE-EARTH METALS

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SHIFTED HOMOLOGOUS RELATIONSHIPS BETWEEN
THE TRANSPLUTONIUM AND EARLY RARE-EARTH METALS*

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ABSTRACT

The physico-chemical properties of the late actinide metals americium through einsteinium are compared with their rare-earth counterparts. Localization of the 5f electrons beginning at americium signals the appearance of true rare-earth-like properties, but the homologous relationship is shifted to place americium below praseodymium, einsteinium then below europium. The comparison of crystal structure, phase transitions, vapor pressures and heats of vaporization reveals remarkable similarities, especially for Sm-Cf and Eu-Es, where the stability of the divalent metal becomes established and divalent chemistry then follows.

There is of course a major perturbation at the half-filled shell at curium, and it may be argued that americium is the anomaly in the so-called second rare-earth series. However, the response of americium, berkellium and californium under pressure reveals the true perturbation to be a thermodynamic one, occurring at curium.

The onset of 5f electron localization in the actinides is probably first seen in the higher temperature phases of plutonium, particularly the fcc delta phase, with a metallic radius of 1.64 Å and a rare-earth-like X-ray adsorption-emission response. Nevertheless, no magnetism is observed, and the radius is still small compared to the rare-earth metals. 5f bonding returns with vengeance in the epsilon and liquid phases, producing (as with neptunium) a very low melting point and a liquid with extremely high viscosity and high boiling point.

The mystery continues with americium, where a major localization and f-band narrowing occurs but magnetism is again quenched by the "magic" 5f electronic configuration; this peculiar non-magnetic ground-state also allows americium to become superconducting, like

*Worked performed under the auspices of the U.S. Department of Energy
Chemically americium is clearly a trivalent metal. The
divalent state is only stabilized by a large ligand such as \( \text{I}^- \);
tetraivalence occurs with strong oxidizing agents \( \text{O}_2, \text{F}_2 \) because the 5f
electrons, though localized, are very close (<2eV) to the Fermi level.
Crystal structures are like those of the early rare-earths - dhcp at
room temperature and fcc at higher temperatures. High-pressure\( ^3 \)
transform the lattice first to an fcc structure (as do the rare-earths),
then to an exotic double body-centered monoclinic phase, and then
finally to an \( \alpha \)-uranium-type structure in the range 15-20 GPa, again
showing the proximity of the 5f electrons to the Fermi level.

The dhcp room temperature and fcc high temperatures are also found
for cerium, and also the elements berkelium and californium, in marked
contrast to the supposed homologs directly above these elements in the
periodic table. A suggestion first noted by Johansson\( ^4 \) shifts the
homologous relationship to place americium below praseodymium, then
comparing the two series as chemical and structural homologs. This
comparison is illustrated in Table 1. The f-bonded early actinides are
grouped for convenience under plutonium, which becomes the homolog for
(the f-bonded collapsed \( \alpha \)-phase of) cerium. It should be noted that
cerium is often used as a stand-in for plutonium, where radioactive
contamination must be avoided.

Americium then becomes the homolog for praseodymium, as noted
above. Both metals can be oxidized to the dioxide, due to the proximity
of the f-energies to the Fermi level. A heat of vaporization for \( \text{Pr} =
85.0 \text{ kcal/mol} \) may be compared with 67.9 kcal/mol for \( \text{Am} \), as measured by
Ward and coworkers (5,6) on both the \( ^{241} \text{Am} \) and \( ^{243} \text{Am} \) isotopes; these
data are shown in Fig. 1. A long-standing controversy between the
measured and theoretical values for the heat of vaporization has recent-
ly been resolved by a new spectroscopic value for the lowest level of
the \( ^6 \text{f}^2 \ \text{Am} \) configuration, thus finally bringing the theoretical
calculations into harmony with experiment. Various theoretical treat-
ments\( ^4,7-10 \) have had considerable success in predicting the cohesive
energies (\( \Delta H \) of vaporization) for the rare-earths, failing for the early
actinides because of no viable model for the itinerant and bonding
3f-electrons. These correlations are based on the spectroscopic values for the gas and the heat of solution; it might therefore be expected that reasonable estimates would be made for the elements americium and beyond, where 5f-bonding no longer is in the picture. This indeed turns out to be true, with the resolution of the americium calculation just discussed.

It can be seen immediately that a major perturbation in the homologous relationship in Table 1 occurs at curium, because of the half-filled shell effect. Is curium like neodymium or gadolinium? Crystal-structure-wise the former is true; in terms of a heat of vaporization \((\text{Cm} = 92.2 \text{ kcal/mol}, \text{Gd} = 95.0 \text{ kcal/mol}, \text{Nd} = 73.3 \text{ kcal/mol})\) the latter seems to be true. However, the "problem" is not really a problem at all; the argument is simply a thermodynamic one, since the half-filled shell stabilizes the trivalent \(\text{Cm(Gd)}\) gas. In terms of solid-state properties, the homologous relationship remains \(\text{Cm-Nd}\).

For the elements beyond plutonium, measurements of the heat capacity are difficult-to-impossible, due to the intense radioactivity and/or vanishingly-small quantities for experiment. Ward and Hill\(^\text{11}\) have established a correlation relating the crystal entropy \(S^\circ_{298}\) to metallic radius, atomic weight, magnetic properties and electronic structure. This correlation permits estimation of reliable entropy values for metals for which no data are available, based on comparison with a closely-similar metal for which there are measured data. The early actinides cannot be assessed by this correlation, because there is no model (as for the theoretical calculation) to account for the complex 5f-electron bonding. However, success is expected and realized for the metals americium and beyond. The estimated value for the correlation for americium of 13.2 cal./mol/K has been precisely confirmed recently by experiments on the \(^{243}\text{Am}\) isotope.\(^\text{12}\)

Noteworthy is the large change of entropy (4.13 cal/K/mol) upon vaporization of Am from the trivalent non-magnetic solid to the divalent magnetic gas. It should be noted that all of the actinide gases are fully magnetic, like the rare-earths, as shown in Fig. 2. Perhaps this should be obvious, but interesting is the fact that simple subtraction
of the magnetic entropies results in a good non-magnetic baseline, except for curium, where there are many low-lying excited states.

The importance of the crystal entropy lies in the fact that the $S_{298}^0$ value is the basis point for the free-energy functions for both the solid and gas. From a reasonably accurate estimate for the solid entropy, the gaseous spectroscopic data and precise vapor pressure measurements, it is possible to calculate all the thermodynamic functions for the metal up to the highest temperatures of measurement. These values have been recently tabulated in the Metals Chapter of the "Handbook for the Physics and Chemistry of the Actinides".\textsuperscript{13}

Unfortunately there exist as yet no data for the rare-earth element promethium, so a comparison with berkelium cannot easily be made. However, it is expected on the basis of the regularity seen elsewhere that the comparison will be excellent. In the measurement of the vapor pressure of pure berkelium-249 metal\textsuperscript{14} neodymium was used as the comparative element for the entropy correlation, correcting of course for the proper magnetic entropies, and the fit was excellent. The measured heat of vaporization of 74.1 kcal/mol may be compared with that for neodymium of 78.3 kcal/mol, with the expectation that the the value for promethium, when finally measured, will be lower.

The comparison at samarium/californium is especially revealing. Incipient stabilization of the divalent state is seen in both metals, with divalent chemical compounds easily formed. The surface of samarium metal has been shown to be divalent\textsuperscript{15}, and there was some question in the early stages of californium metal studies whether the metal was divalent. However, the thermodynamic data\textsuperscript{16} clearly establish californium to be a trivalent metal but with a heat of vaporization of only 46.9 kcal/mol (as compared to 49.4 kcal/mol for samarium) and with a vapor pressure midway between that for samarium and europium, as shown in Fig. 3.

Recent Henry's-Law vaporization studies of einsteinium-253 dissolved in ytterbium show\textsuperscript{9,17} the metal to be clearly divalent, with a heat of vaporization of only 31.8 kcal/mol (similar to strontium), thus completing the homologous miniseries by analogy to divalent europium.
Some comparative properties of the early lanthanides and late actinides are summarized in Table 2. Trends in cohesive energies are illustrated by the measured heats of vaporization of the actinide metals, plotted in Fig. 4.

Beyond einsteinium there is no corresponding half-filled shell in the actinide series, and the divalent state will continue to be the preferred electronic configuration for the metals fermium and beyond. At the moment, half-lives are too short and quantities too small for meaningful bulk measurements beyond einsteinium.

Thus in summary, a shifted homologous relationship exists for the transplutonium actinides, resulting in the miniseries Am-Em corresponding to the series Pr-Eu. The half-filled shell at Cm introduces a thermodynamic complication which is however not reflected in the condensed phase properties of this element.

REFERENCES


COMPARATIVE PHYSICOCHEMISTRY OF LANTHANIDES AND ACTINIDES
(THE "JOHANSSON SHIFT")

La Ce+ Pr Nd Pm Sm Eu* Gd Tb

Ac Pu Am Cm Bk Cf Es* Cm

half-filled shell

f-bonding

f-bonding in the collapsed phase

* divalent
Table 2. Comparative Values for the Actinides Am-Es and Lanthanides Pr-Eu

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal</th>
<th>M.P. (K)</th>
<th>B. P. (Cal/K/Mol)</th>
<th>$C^\circ_p$ (Cal/K/mol)</th>
<th>$S^o_{298}$ (Cal/K/mol)</th>
<th>$\Delta H^o_{298}$ (kcal/Mol)</th>
<th>Chemistry</th>
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<td>Pair(s)</td>
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<td>~2220</td>
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<td>(dhcp, bcc)</td>
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<td>3539</td>
<td>(Pt)</td>
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<td>2730(?)</td>
<td></td>
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<td>6.48</td>
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<td>41.9</td>
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</table>

[ ] = other possible valence states

a from the Entropy correlation, Ward & Hill (11)
Figure Captions

1. Vapor pressure data for americium. The heavier line represents 37 data points taken with the 241 isotope (Ref. 5); extent of range is indicated by small arrows. Data points and the lighter line represent values with the 243 isotope, extending into the liquid range: ◆ Los Alamos data; □ Karlsruhe data (Ref. 6).

2. Comparison of gaseous entropies for the lanthanides and actinides at 298K and 1400K. ◆ divalent (d") curve for the lanthanides; ● trivalent (d") gases; ▼ fully magnetic actinide gas; ▼ non-magnetic portion of entropy for each element.

3. Vapor pressure of solid californium, compared to data for samarium and europium (Ref. 16). Target data ◆ and mass spectrometric data were taken, stately with a 2 mg sample of pure 249 Cf (tailoff for the highest points was due to incipient sample depletion).

4. Comparative plot of the cohesive energies of the actinide metals, in kJ/mol (left ordinate) or kcal/mol (right ordinate). Open data point at Pa represents a still-unresolved uncertainty for this element.
"Non-mag" baseline (4f) II

"Non-mag" baseline (5f)
$M(s, l)$ to $M(g)$

kJ/mol

Th U Pu Np Am Bk Cf Es

kcal/mol

Fig. 4