FRONTIERS OF CHEMISTRY FOR AMERICIUM AND CURIUM*

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ABSTRACT. The discoveries of americium and curium were made only after Seaborg had formulated his actinide concept in order to design the chemistry needed to separate them from irradiated ^{239}Pu targets. Their discoveries thus furnished the first clear-cut evidence that the series exists and justified Seaborg's bold assumption that even though Th and Pa appeared to presage a following 6d series, the pattern established by the periodic table after Cs and Ba would be repeated exactly after Fr and Ra. That is to say, a new 5f element rare earth series (the actinides) would follow Ac in the same way the 4f rare earth series (the lanthanides) follows La. The consequences of the resulting half-filled $5f^7$ shell at Cm were originally presented by Seaborg as a test of his hypothesis. Recent research is outlined that substantiates Seaborg's predictions in new and definitive ways.

Americium and curium are of historic importance in chemistry because the method used in their discovery by Seaborg, Ghiorso and co-workers furnished the first clear-cut evidence that the actinide series exists. And, as is evident in this Symposium, americium and curium are still furnishing insights into the systematics and the underlying electronic phenomena implied by the formulation of the periodic table on the basis of the actinide concept.

As everyone knows, scientists often assume the validity of some pattern when they set up their own experiments. In his first attempts to discover Am and Cm, Seaborg (1) made the reasonable assumption that the pattern of chemical properties set up by U, Np, and Pu would persist to elements 95 and 96. The nuclear reactions employed in these new element discovery experiments were the bombardment of plutonium-239 with alpha-particles to produce ^{242}Cm and with neutrons to produce ^{241}Pu which would then decay to ^{241}Am. The chemical separations of Am or Cm from the irradiated ^{239}Pu targets were then based on the idea that they

would be fairly readily oxidizable to the VI state to ions analogous to PuO_2^{2+}. The experiments based on this assumption did not bear fruit, and it became apparent that some new tack had to be taken.

There were also, of course, various assumptions about the untried nuclear reactions that were used in these unsuccessful attempts to produce Am and Cm from the ^{239}Pu target. But Seaborg assumed correctly that the assumptions about the chemistry were what needed changing.

In his first attempts to predict the chemistry of Am and Cm, Seaborg chose as a guide a very simple pattern – namely, a direct extrapolation from the properties of U, Np, and Pu. When this approach did not work, he then made the very bold assumption that even in this heavy element region it was possible to take the regularity set by the periodic table in the lighter elements quite literally (Figure 1). If the pattern established by the periodic table after Cs and Ba were repeated in exactly the same way after Fr and Ra, then a new 5f element rare earth series (the actinides) would follow Ac in the same way the 4f rare earth series (the lanthanides) follows La. If such a 5f rare earth series were actually following Ac – but the apparent analogy with the lanthanides was not really going to be apparent until Am and Cm – then these new undiscovered elements should have chemical properties similar to Eu and Gd rather than U, Np, and Pu. Even though we have had the opportunity to look in the back of the book and see the answer, the assumptions that led Seaborg to his new formulation of the periodic table look bold even today, and it is rare indeed that anyone has such penetrating insights on the basis of only the scanty evidence that was available at the time.

In making the assumption that the straightforward regularity of the periodic table would become apparent once again at Am and Cm, Seaborg had very little guidance from either experiment or theory (2). Th and Pa, the first two elements after Ac, behave chemically very much like Hf and Ta, the first two members of the 5d transition series. Thus it was natural to assume that Th and Pa were the first two members of the 6d transition series. On the other hand, work in the wartime Manhattan Project was helpful in showing that something new was going on in the U, Np, and Pu region because Np and Pu bear no resemblance to Re and Os, and the chemistry of U differs in important ways from the chemistry of W. Also, although theory did not offer any concrete evidence either, several computations made in the 30's and early 40's did suggest that 5f electrons could be stabilized versus 6d in the U/Pu region (2,3).

In spite of the extreme skepticism expressed by his colleagues about the possible validity of the proposed actinide concept, Seaborg went ahead and designed a new chemical scheme on the basis of it for separating Am and Cm from the irradiated ^{239}Pu targets. His tenacity paid off because he, Ghiorso, and their colleagues quickly met with success. The initial evidence for the validity of the actinide concept was thus established by nature of the chemistry employed in the new element discovery experiments for Am and Cm.

In his 1945 article (4) describing the discovery of Am and Cm and his formulation of the actinide series, Seaborg laid special stress on the testing of his hypothesis through the extra stability that would be

imparted to the III oxidation states of elements 96 and 103 by the half filled $5f^7$ and filled $5f^{14}$ shells that should occur in them if <u>actinium</u> really is the first member of a postulated new 5f rare earth series. He mentioned several times in the article, in fact, that Cm should exhibit the III state almost exclusively because of its $5f^7$ half filled shell.

Experimental determination of the extra chemical stability of the III oxidation state of curium relative to americium and berkelium furnished important early support for the actinide concept. Of parallel interest, but much later, it was shown also by R. J. Silva and co-workers (5) that Lr has a most stable oxidation state of III as predicted by Seaborg for the last member of the actinide series. This experiment on Lr (the only chemical one that has ever been performed on this element) was particularly important since shortly before it was done the surprising discovery had been made by Maly, Sikkeland, Silva, and Ghiorso that No, the second to the last member of the series, is most stable in the divalent state (6).

Although no additional chemical experiments have been possible yet with Lr, several types of experiments have demonstrated the extra stability of the trivalent state in Cm that Seaborg predicted. A good example is the heat of sublimation of Cm over that of Am and Bk. This effect is shown from data of Kleinschmidt, Ward, and Haire (7) in Figure 2. Their value of the heat of sublimation for Lr was predicted on the basis of its trivalency, which has already been established for the trivalent ion in aqueous solution as noted above. The low heats of sublimation of Fm, Md, and No were predicted on the basis of their expected divalency. Actually, the divalency of Fm and Md has been demonstrated experimentally already by the gas chromatography results of Hubener and Zvara (8) and there can be little doubt that No is divalent. So the heat of sublimation of Lr will be a most important quantity to measure. It may actually be much lower than predicted by Kleinschmidt and coworkers because, although Lr is trivalent in aqueous solution, the electronic configuration of the metal may be different from what would be predicted on the basis of analogy with Lu. Strong relativistic effects in the Lr region will definitely stabilize the $7s^2$ closed shell more than the $6s^2$ closed shell in Lu, and they also could cause the replacement of the expected 6d electron, which is very interactive, with a $7p_{1/2}$ electron, which is relatively inert. These two effects could work in conjunction to lower the heat of sublimation of Lr substantially (9).

Fortunately, it has become possible recently to experimentally demonstrate in a direct manner the extra stability of the highly localized $5f^7$ shell in curium. In essence, the approach is to test the stability of the f shells in transplutonium metals by placing them under a high enough pressure that they delocalize into the spd bands. That is to say that the pressure is high enough to cause the f electrons to change from a localized non-bonding character into a delocalized bonding character. A recent review has been given by Benedict (10).

All four of the metals – Am, Cm, Bk, and Cf – now have been studied (11,12,13). An illustration using results from a paper by Roof, Haire and coworkers (13) is given in Figure 3. In this experiment, Am metal

ultimately assumes the alpha uranium structure which is associated with fspd hybridization.

Thus the high pressure technique gives an ideal way to determine f orbital stability because the more stable the orbitals, the higher the pressure required to bring about their delocalization. The results for the four metals Am, Cm, Bk, and Cf are given in Figure 4 (14). Since the pressure required to delocalize the f orbitals in Cm is much higher than in Am or Bk, its extra stability is clearly shown. Thus the stability of the f shell in Cm is demonstrated directly and its position as the middle member of the actinide series is verified in a most definitive way.

Another verification of the actinide concept comes from the discovery by J. L. Smith and R. G. Haire (15) of superconductivity in Am metal. The superconductivity is allowed in Am metal because it has a nonmagnetic ground state like La, which is also a superconductor. But the important point for adding to our understanding of the systematics of the actinide series is that Am metal is trivalent and nonmagnetic because it has a unique f^6 configuration in the ground state. Even europium, americium's homologue in the lanthanide series, does not exhibit the f^6 configuration in the metal (as shown by its divalency) and is not superconducting. Smith and Haire point out also that the f electron character in Am and La must be important in allowing superconductivity since other trivalent elements that do not have available f orbitals are not superconducting. Studies of Am superconductivity under high pressures should be most enlightening in elucidating the role of f orbitals in this phenomenon, and hopefully we will be treated to the results of such experiments in the near future.

The discovery of Am and Cm was especially useful for developing an understanding of the underlying 5f electronic properties of the series because they introduced a simplicity that was not offered by U, Np, and Pu. But suppose, for example, that Am had turned out to be divalent like No! Then it would have been even more difficult to discover Am although, fortunately, Cm would still have saved the day. Actually, even with the simplicity introduced by the discovery of Am and Cm, there was still enough confusion that many scientists provisionally classified the elements Th through Cm as both sub-group elements and as a second rare earth series at the same time. One of the scientists who did that was Seaborg himself (Figure 1). But within a few years it became obvious that Seaborg was correct in placing them as a second rare earth series and the sub-group classification disappeared.

Certainly a key result of the efforts of transuranium chemists over the last 40 years has been the validation and elucidation of the actinide concept. As we move ahead into further investigations of the architecture of the periodic table through chemical studies of Lr, the first members of the transactinide series and beyond, we are fortunate to have as a guide the valuable lessons from the work of Seaborg and his coworkers in those exciting early days of the discovery of Am and Cm.

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FIGURE CAPTIONS

Figure 1. Caption on Figure. Please add under figure "Reprinted with permission from Ref. 4. Copyright 1945, American Chemistry Society".

Figure 2. Heats of Sublimation of Actinide Metals (Data from Ref. 7).

Figure 3. Phase Changes and Delocalization of f orbitals in Am metal under pressure (Ref. 13).

Figure 4. Half-filled shell stabilization of Cm metal shown by anamalously high pressure for f orbital delocalization (Ref. 14).

PERIODIC TABLE SHOWING HEAVY ELEMENTS AS MEMBERS OF AN ACTINIDE SERIES

Arrangement by Glenn T. Seaborg

1945

1 H 1.008																	1 H 1.008	2 He 4.003
3 Li 6.940	4 Be 9.02												5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.997	12 Mg 24.32	13 Al 26.97											13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944
19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38		31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.880	48 Cd 112.41		49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3
55 Cs 132.91	56 Ba 137.36	57 La / 58-71 Lu series		72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po	85	86 Rn 222
87	88 Ra	89 Ac / 90-96 Ac series		90 Th	91 Pa	92 U	93 Np	94 Pu	95	96								

LANTHANIDE SERIES	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

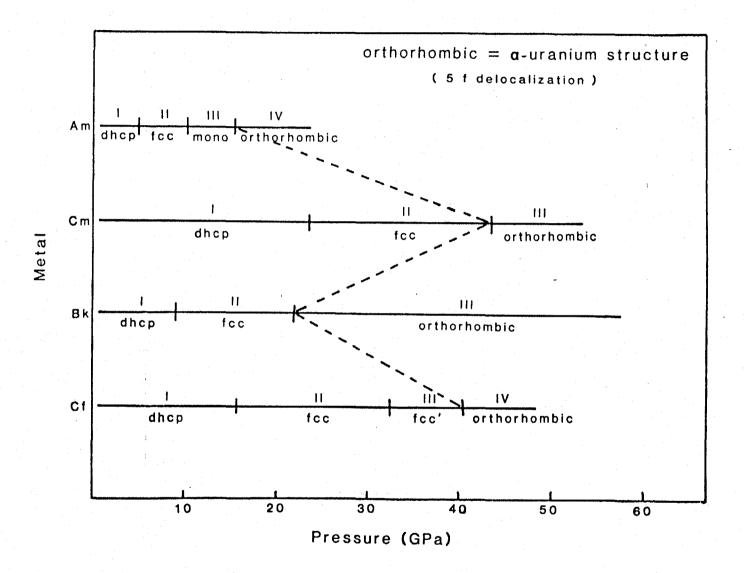| ACTINIDE SERIES	89 Ac	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np 237	94 Pu	95	96							

Fig 1

Fig 2

ORNL DWG 83-10047

Fig 3

Fig 4