

Heavy Element Chemistry Portfolio

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Heavy Element Chemistry Portfolio

- ◆ **Fundamental understanding of bonding and reactivity of the actinides, especially properties related to presence of 5f electrons.**
 - Elements through Cf at \geq microgram scale; short-lived isotopes with tracers.
 - Synthesis
 - Chemical bonding and speciation
 - Coordination and environmental chemistry
 - Theoretical methods to calculate electronic properties, molecular structure, and reactivity
- ◆ **Bonding and reactivity of Np, Pu, Am, and Tc to control environmental consequences of release of radioisotopes**
- ◆ **Chemical properties of the transactinides, developing new techniques for nuclei with half-lives of seconds to tens of seconds.**
- ◆ **Support summer radiochemistry programs for undergraduate students (grant with oversight by ACS).**

The Actinide Challenge: Understanding 5f Electron Behavior

Depending on chemical surroundings, temperature, applied magnetic field, and pressure, *f* electrons vary from being atomic-like, i.e., localized to a particular site, to being band-like, i.e., spreading their wavefunction out over the entire system. The *f* electrons in some materials are localized at room temperature but can become superconducting at low temperature.

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89 Ac Actinium	104 Rf Rutherfordium	105 Ha Hahnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112	113	114	115	116		

Lanthanide series

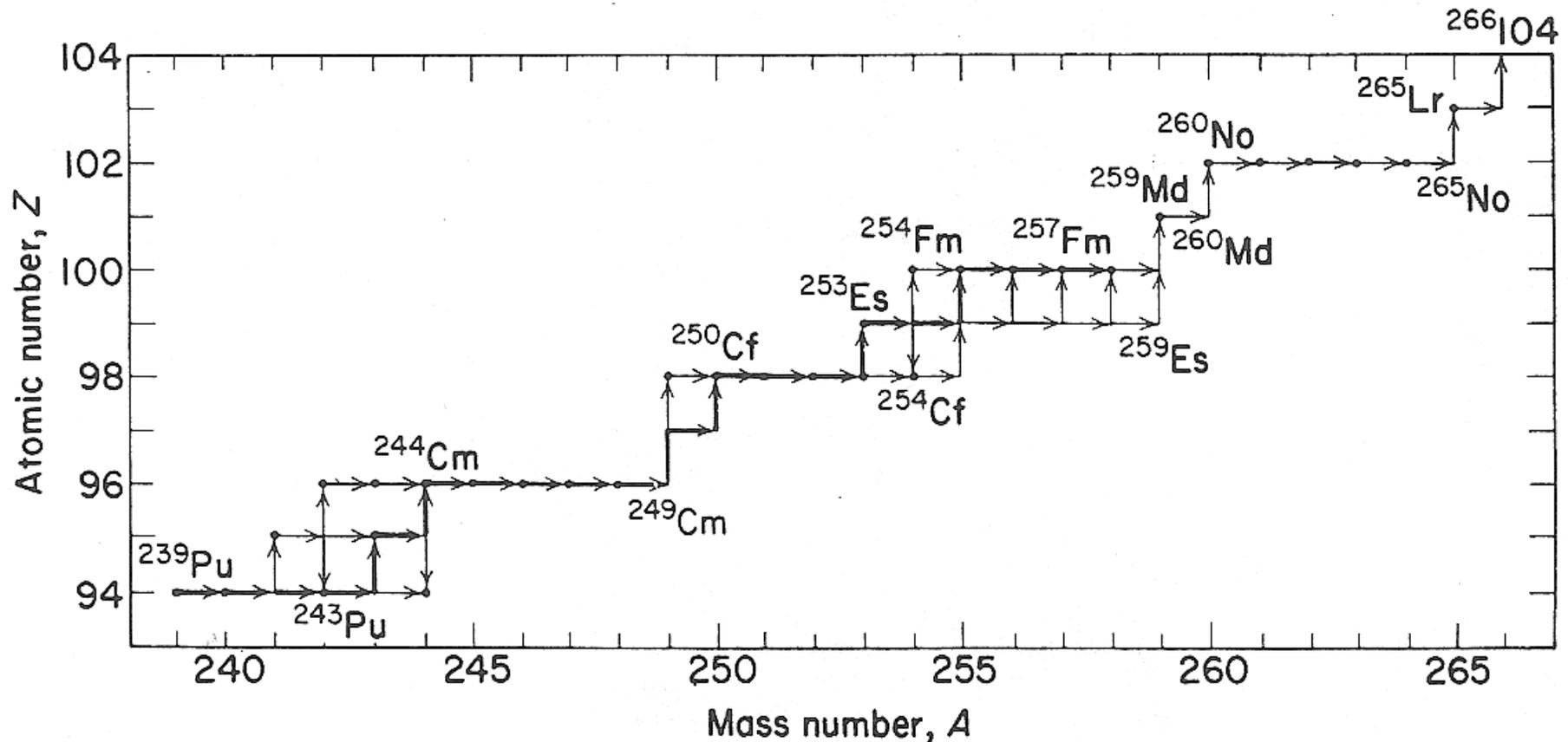
58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
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Actinide series

90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium
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Actinide elements important in the closed nuclear fuel cycle

Production of transplutonium elements by slow-neutron irradiation



Nuclear reaction sequence for production of transplutonium elements by intense slow-neutron irradiation. The principal path is shown by heavy arrows (horizontal, neutron capture; vertical, beta decay). The sequence above ^{258}Fm is a prediction.

Production of transcurium isotopes in USA^a

Isotope	Half-life	Amount/year, 1983	Amount/campaign, 2003
²⁴⁸ Cm	3.48 x 10 ⁵ yr	150 mg ^b	100 mg ^b
²⁴⁹ Bk	330 d	50 mg	45 mg
²⁴⁹ Cf	351 yr	50 mg ^c	<45 mg ^c
²⁵² Cf	2.645 yr	500 mg	400 mg
²⁵³ Es	20.47 d	2 mg ^a	1-2 mg ^d
²⁵⁴ Es	275.7 d	3 μg	4 μg
²⁵⁷ Fm	100.5 d	1 pg	1 pg

^a One or two separation campaigns per year until about 1995; one campaign every 18-24 months from about 1995 to 2003.

^b From α decay of ²⁵²Cf.

^c From β decay of ²⁴⁹Bk.

^d Mixed with 0.06-0.3% ²⁵⁴Es; chemical separation of ²⁵³Cf followed by its β decay can yield ~200 μg of isotopically pure ²⁵³Es.

Ion types and colors for actinide ions in aqueous solution

Element	M^{3+}	M^{4+}	MO_2^+	MO_2^{2+}	$MO_4(OH)_2^{3-}$ (alkaline soln)
actinium	colorless				
thorium		colorless			
protactinium		colorless	colorless		
uranium	red	green	color unknown	yellow	
neptunium	blue to purple	yellow-green	green	pink to red	dark green
plutonium	blue to violet	tan to orange	reddish-purple	yellow to pink-orange	dark green
americium	pink or yellow	color unknown	yellow	rum-colored	
curium	pale green	color unknown			
berkelium	green	yellow			
californium	green				

Ionic radii of lanthanides and actinides (coordination number 6) (Shannon, 1976)

No. of 4f or 5f electrons	Lanthanide series						Actinide series					
	2+ ion	Radius (Å)	3+ ion	Radius (Å)	4+ ion	Radius (Å)	2+ ion	Radius (Å)	3+ ion	Radius (Å)	4+ ion	Radius (Å)
0			La ³⁺	1.032	Ce ⁴⁺	0.87			Ac ³⁺	1.12	Th ⁴⁺	0.94
1			Ce ³⁺	1.01	Pr ⁴⁺	0.85			Th ³⁺		Pa ⁴⁺	0.90
2			Pr ³⁺	0.99					Pa ³⁺	1.04	U ⁴⁺	0.89
3			Nd ³⁺	0.983					U ³⁺	1.025	Np ⁴⁺	0.87
4	Nd ²⁺	1.20 ¹	Pm ³⁺	0.97					Np ³⁺	1.01	Pu ⁴⁺	0.86
5			Sm ³⁺	0.958					Pu ³⁺	1.00	Am ⁴⁺	0.85
6	Sm ²⁺	1.18 ¹	Eu ³⁺	0.947					Am ³⁺	0.975	Cm ⁴⁺	0.84
7	Eu ²⁺	1.17	Gd ³⁺	0.938	Tb ⁴⁺	0.76	Am ²⁺	1.16 ¹	Cm ³⁺	0.97	Bk ⁴⁺	0.83
8			Tb ³⁺	0.923					Bk ³⁺	0.96	Cf ⁴⁺	0.821
9			Dy ³⁺	0.912					Cf ³⁺	0.95	Es ⁴⁺	0.81
10	Dy ²⁺	1.07	Ho ³⁺	0.901			Cf ²⁺	1.14	Es ³⁺	0.93		
11			Er ³⁺	0.890					Fm ³⁺			
12			Tm ³⁺	0.880					Md ³⁺			
13	Tm ²⁺	1.03	Yb ³⁺	0.868					No ³⁺			
14	Yb ²⁺	1.02	Lu ³⁺	0.861			No ²⁺	1.05	Lr ³⁺			

¹ Corrected to coordination number 6.