Heavy Element Chemistry Portfolio

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DOE Isotopes Workshop
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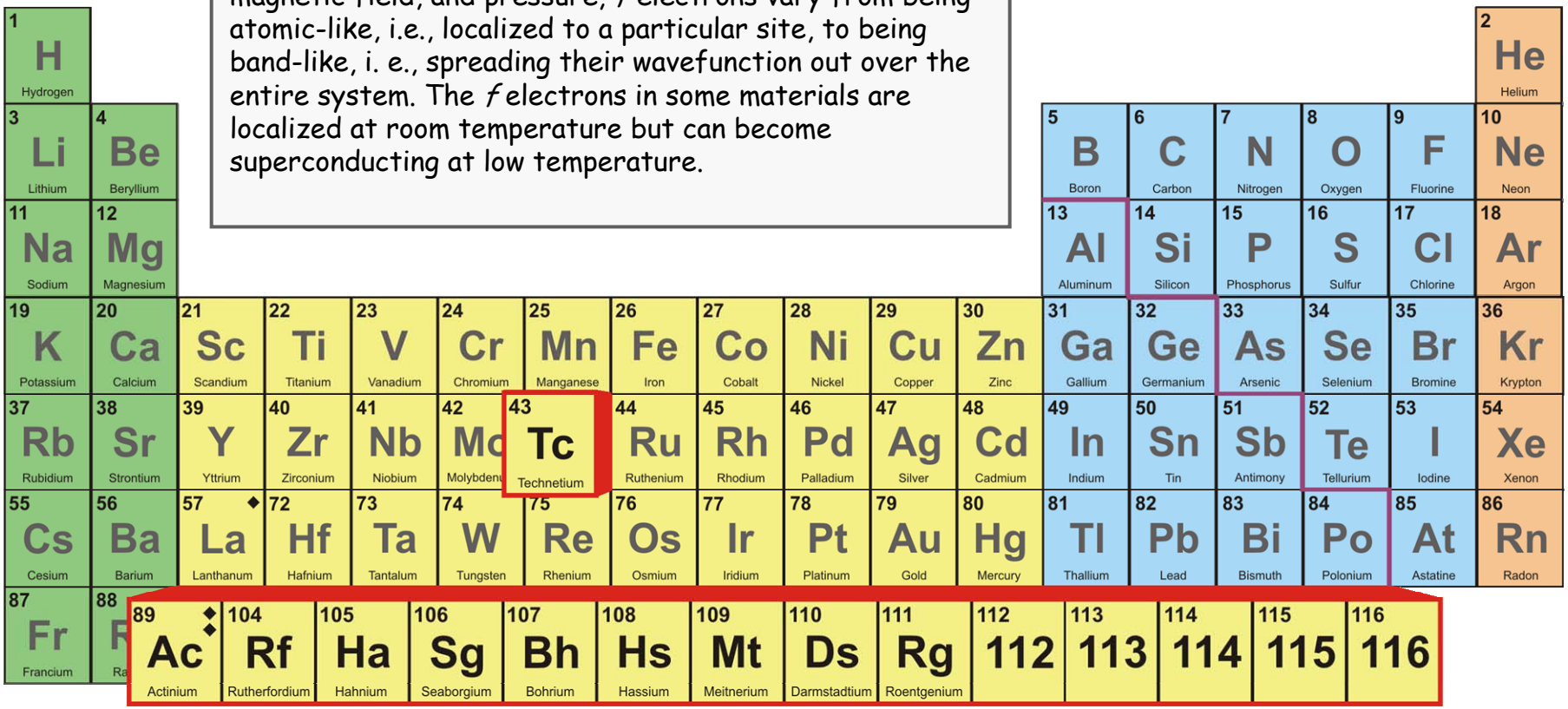
Heavy Element Chemistry Portfolio

- **Fundamental understanding of bonding and reactivity of the actinides, especially properties related to presence of 5f electrons.**
  - **Elements through Cf at ≥ 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).**

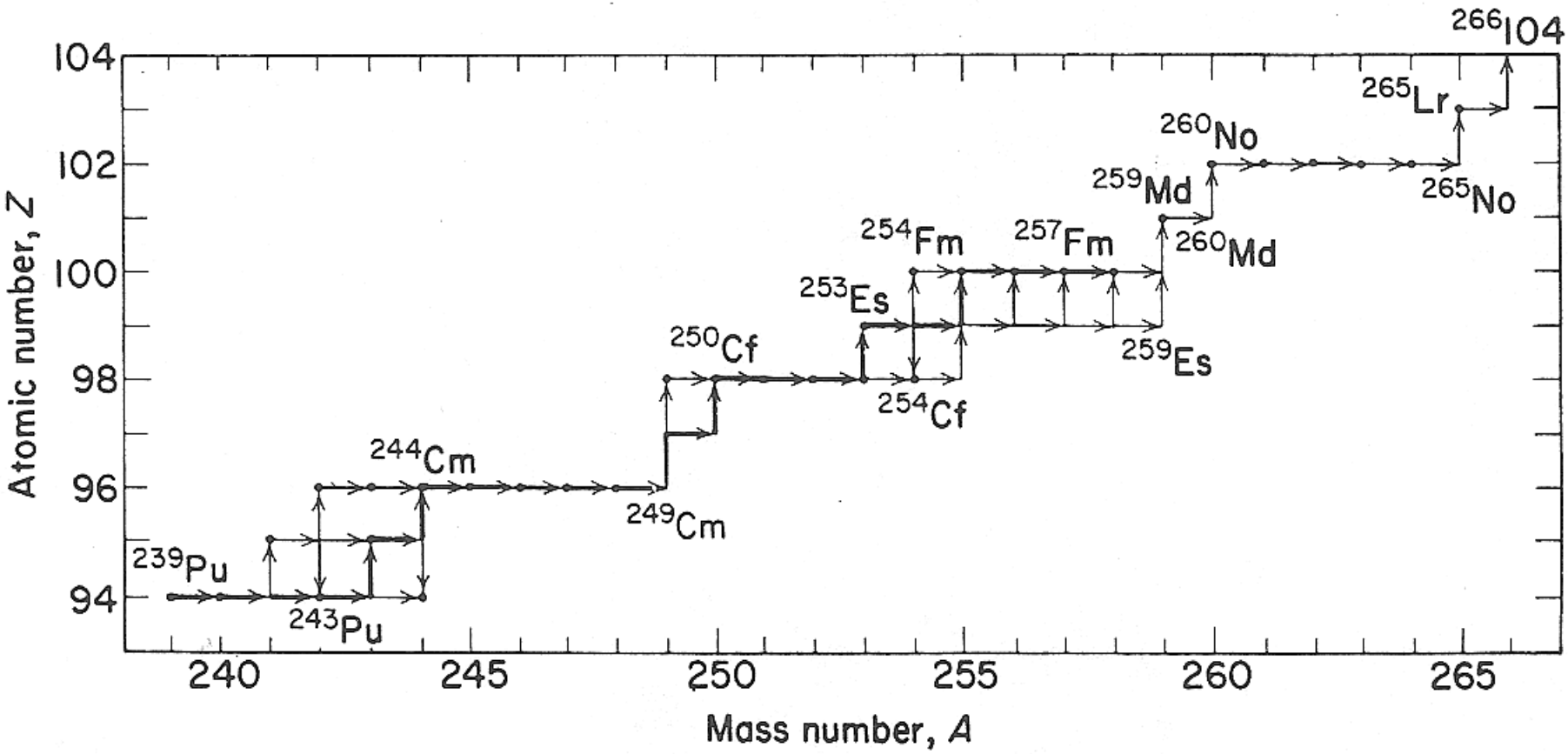
The Actinide Challenge: Understanding 5f Electron Behavior

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.



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 ^{252}Cf.
[c] From β decay of ^{249}Bk.
[d] Mixed with 0.06-0.3% ^{254}Es; chemical separation of ^{253}Cf followed by its β decay can yield ~200 μg of isotopically pure ^{253}Es.

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 un-known	yellow	
neptunium	blue to pur-ple	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 yel-low	color un-known	yellow	rum-colored	
curium	pale green	color un-known			
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.