

Lecture 5

ACTINIDE SERIES

(5f- elements)

4th year (Micro/Chem- Botany/Chem and
Biochemistry)

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What are Actinides?

- the second inner transition series
- It contains the elements with atomic numbers 89-103, in which the **5f** orbitals are being filled up (the extra electron enters the 5f-orbital).
- the elements of this series are also called as actinoides or actinones.

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ACTINIDE SERIES

All of them are radioactive



Actinides Properties

1. Occurrence of The Elements

- Only **Actinium, Thorium, Protactinium & Uranium** occur naturally (*i.e.* $Z \leq 92$) in Uranium minerals.
- all the remaining actinides are unstable and made artificially by nuclear transmutations.
- The actinides elements lying **beyond Uranium**, are called **trans-uranium** or **trans-Uranic** elements
- All the actinides are radioactive.
- Silvery in appearance but display a variety of structures due to the irregularity in metallic radii which are far greater than are found in lanthanoids.

General Properties

- 1) The elements are all metals with fairly high melting points though the values are considerably lower than for the transition elements.
- 2) The sizes of the ions decreases regularly along the series because of the poor screening of the nuclear charge by the f- orbital results in an **actinide contraction** similar to the lanthanide contraction.
- 3) The actinides are much more dense.
- 4) They are reactive metals like La and the lanthanons.

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Some characteristic properties of actinides

- The dominant oxidation state of actinides is +3.
- Actinides also exhibit an oxidation state of +4.
- Some actinides such as uranium, neptunium and plutonium also exhibit an oxidation state of +6.

The actinides show **actinide contraction** (like lanthanide contraction) due to poor shielding of the nuclear charge by 5f electrons.

- All the actinides are **radioactive**.
- The radioactive nature of Actinides are make the study of their chemistry is difficult in the laboratory.
- Their chemistry is studied using tracer techniques.

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Properties of Actinides

1. Electronic configuration
2. Oxidation state
3. Ionic size
4. Actinide contraction
5. Magnetic properties
6. Color
7. Complex formation
8. Chemical reactivity of Actinides

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Element	Symbol	A.N	Electronic configuration	An ³⁺	Other Oxidation states
Actinium	Ac	89	[Rn] 6d ¹ 7s ²	[Rn]4f ⁰	
Thorium	Th	90	[Rn]5f ¹ 6d ¹ 7s ²	[Rn]4f ¹	IV
Protactinium	Pa	91	[Rn]5f ² 6d ¹ 7s ²	[Rn]4f ²	IV, V
Uranium	U	92	[Rn]5f ³ 6d ¹ 7s ²	[Rn]4f ³	IV, V, VI
Neptunium	Np	93	[Rn]5f ⁴ 6d ¹ 7s ²	[Rn]4f ⁴	IV, V, VI, VII
Plutonium	Pu	94	[Rn]5f ⁶ 7s ²	[Rn]4f ⁵	IV, V, VI, VII
Americium	Am	95	[Rn]5f ⁷ 7s ²	[Rn]4f ⁶	IV,VI
Curium	Cm	96	[Rn]5f ⁷ 6d ¹ 7s ²	[Rn]4f ⁷	IV
Berkelium	Bk	97	[Rn]5f ⁹ 7s ²	[Rn]4f ⁸	IV
Californium	Cf	98	[Rn]5f ¹⁰ 7s ²	[Rn]4f ⁹	IV
Einsteinium	Es	99	[Rn]5f ¹¹ 7s ²	[Rn]4f ¹⁰	II
Fermium	Fm	100	[Rn]5f ¹² 7s ²	[Rn]4f ¹¹	II
Mendelevium	Md	101	[Rn]5f ¹³ 7s ²	[Rn]4f ¹²	II
Nobelium	No	102	[Rn]5f ¹⁴ 7s ²	[Rn]4f ¹³	II
Lawrencium	Lr	103	[Rn]5f ¹⁴ 6d ¹ 7s ²	[Rn]4f ¹⁴	

1. Electronic Configuration

- All the actinides have common $7s^2$ configuration and variable occupancy of 5f and 6d sub shells.
- The general electronic configuration of actinides is

$$[\text{Rn}] 5f^{0-14}6d^{0-1} 7s^2$$
- The irregularities in the electronic configuration are related to the stabilities of **half filled** or **full filled** orbitals (f^0, f^7, f^{14}).

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2. Oxidation States:

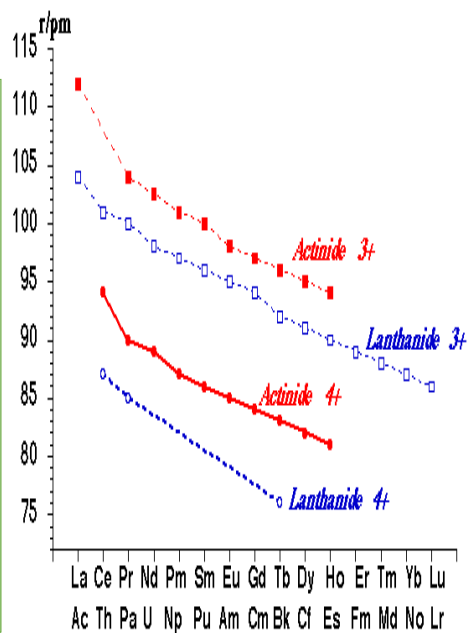
- Unlike lanthanides, actinides show a variety of oxidation states from +3 to +6 due to the very small energy gap between 5f, 6d and 7s sub shells.
- The principal oxidation states are +3 and +4.
- The +3 oxidation state is the most stable.
- The +4 oxidation state is the most stable in Th and Pu.
- +5 in Pa and Np and +6 is seen in U.
- In actinides, the distributions of oxidation states are uneven.

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3. Ionic sizes

Ionic radius

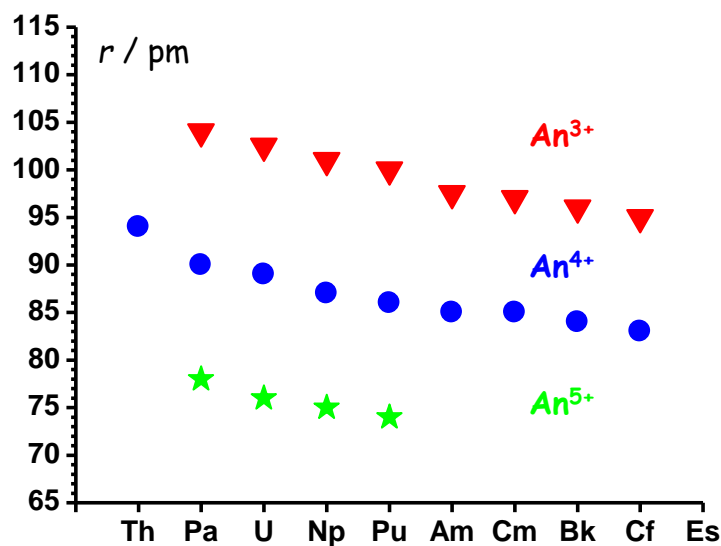
The ionic radius of actinides decreases regularly along the series. The decrease in ionic radius of actinides is called **actinides contraction**, and is due to the poor screening effect of the nuclear charge by the *f* electrons.



Actinide Contraction

- The size of atoms or M^{3+} ions decrease regularly along the actinides series with increase in atomic number from Th to Lr.
- The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction just like lanthanide contraction.

Ionic radii: actinide contraction



4. Magnetic properties

Magnetic behavior:

- All actinides are **paramagnetic** in nature which depends on the presence of unpaired electrons.
- Magnetic properties are more complex than those of lanthanoids.
- Ligand field effects are expected where 5f orbitals are involved in bonding.

5. Color

- Actinides ions are usually colored.
- The color depends upon the number of 5f electrons,
- ions with $5f^0$ electrons and $5f^{14}$ electrons are colorless.
- The color is due to f-f electronic transitions.
- Most of the tri positive and tetra positive (3+ and 4+) ions are colored.

Example:

Ac³⁺ - colorless,
 Np³⁺ - Purple,
 Am³⁺ - pink,
 Cm³⁺ - colorless, U⁴⁺ -
 Green,
 Np⁴⁺ - Yellow-green.

Approximate colors of actinide ions in aqueous solution^[82]

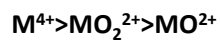
Oxidation state	89	90	91	92	93	94	95	96	97	98	99
+3	Ac ³⁺	Th ³⁺	Pa ³⁺	U ³⁺	Np ³⁺	Pu ³⁺	Am ³⁺	Cm ³⁺	Bk ³⁺	Cf ³⁺	Es ³⁺
+4		Th ⁴⁺	Pa ⁴⁺	U ⁴⁺	Np ⁴⁺	Pu ⁴⁺	Am ⁴⁺	Cm ⁴⁺	Bk ⁴⁺	Cf ⁴⁺	
+5			PaO ₂ ⁺	UO ₂ ⁺	NpO ₂ ⁺	PuO ₂ ⁺	AmO ₂ ⁺				
+6				UO ₂ ²⁺	NpO ₂ ²⁺	PuO ₂ ²⁺	AmO ₂ ²⁺				
+7					NpO ₂ ³⁺	PuO ₂ ³⁺	[AmO ₆] ⁵⁻				

Electronic Spectra

- Narrow bands (compared to transition metal spectra).
- Relatively uninfluenced by ligand field effects.
- Intensities are ca. 10 x those of lanthanide bands.
- Complex to interpret.

6. Complex formation

- The degree of complex formation decreases in the following order:



- The complexing power of different singly charged and doubly charged anions following order.

