Actinides (actinoids)

Prior to 1940 only naturally occurring Th, Pa and U were known.

In 1789 M. H. Klaproth examined pitchblende, thought at the time to be a mixed oxide ore of zinc, iron and tungsten, and showed that it contained a new element which he named *uranium* after the recently discovered planet, Uranus. Then in 1828 J. J. Berzelius obtained an oxide, from a Norwegian ore now known as “thorite”; he named this *thoria* after the Scandinavian god of war and, by reduction of its tetrachloride with potassium, isolated the metal *thorium*. The same method was subsequently used in 1841 by B. Peligot to effect the first preparation of metallic uranium.
The much rarer element, protactinium, was not found until 1913 when K. Fajans and O. Göhring identified $^{234}\text{Pa}$ as an unstable member of the $^{238}\text{U}$ decay series:

$$^{238}\text{U} \xrightarrow{\alpha} ^{234}\text{Th} \xrightarrow{\beta^-} ^{234}\text{Pa} \xrightarrow{\beta^-} ^{234}\text{U}$$

They named it brevium because of its short half-life (6.70 h). The more stable isotope $^{231}\text{Pa}$ ($t_{1/2} = 32760$ y) was identified 3 years later by O. Hahn and L. Meitner and independently by F. Soddy and J. A. Cranston as a product of $^{235}\text{U}$ decay:

$$^{235}\text{U} \xrightarrow{\alpha} ^{231}\text{Th} \xrightarrow{\beta^-} ^{231}\text{Pa} \xrightarrow{\alpha} ^{227}\text{Ac}$$
In the early years of this century the periodic table ended with element 92 but, with J. Chadwick's discovery of the neutron in 1932 and the realization that neutron-capture by a heavy atom is frequently followed by $\beta^-$ emission yielding the next higher element, the synthesis of new elements became an exciting possibility. E. Fermi and others were quick to attempt the synthesis of element 93 by neutron bombardment of $^{238}\text{U}$, but it gradually became evident that the main result of the process was not the production of element 93 but nuclear fission, which produces lighter elements. However, in 1940, E. M. McMillan and P. H. Abelson in Berkeley, California, were able to identify, along with the fission products, a short-lived isotope of element 93 ($t_{1/2} = 2.355$ days):

\[
\begin{align*}
^{238}_{92}\text{U} + ^1_0\text{n} & \longrightarrow ^{239}_{92}\text{U} \rightarrow ^{239}_{93}\text{Np}
\end{align*}
\]

As it was the next element after uranium in the now extended periodic table it was named *neptunium* after Neptune, which is the next planet beyond Uranus.

Isolation and characterization of the heavier actinoids is not easy:
- Need to separated from other actinoids (similar problems as with lanthanoids because of the chemical similarity)
- Need to be separated from lanthanides (formed as fission products)
- High radioactivity – careful protection
- Minute amounts of material
<table>
<thead>
<tr>
<th>Element</th>
<th>Discoverers</th>
<th>Date</th>
<th>Synthesis</th>
<th>Origin of name</th>
</tr>
</thead>
<tbody>
<tr>
<td>93 Neptunium, Np</td>
<td>E. M. McMillan and P. Abelson</td>
<td>1940</td>
<td>Bombardment of $^{238}\text{U}$ with $^1\text{n}$</td>
<td>The planet Neptune</td>
</tr>
<tr>
<td>94 Plutonium, Pu</td>
<td>G. T. Seaborg, E. M. McMillan, J. W. Kennedy and A. Wahl</td>
<td>1940</td>
<td>Bombardment of $^{238}\text{U}$ with $^1\text{H}$</td>
<td>The planet Pluto (next planet beyond Neptune)</td>
</tr>
<tr>
<td>95 Americium, Am</td>
<td>G. T. Seaborg, R. A. James, L. O. Morgan and A. Ghiorso</td>
<td>1944</td>
<td>Bombardment of $^{239}\text{Pu}$ with $^1\text{n}$</td>
<td>America (by analogy with Eu, named after Europe)</td>
</tr>
<tr>
<td>96 Curium, Cm</td>
<td>G. T. Seaborg, R. A. James and A. Ghiorso</td>
<td>1944</td>
<td>Bombardment of $^{239}\text{Pu}$ with $^2\text{He}$</td>
<td>P. and M. Curie (by analogy with Gd, named after J. Gadolin)</td>
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<tr>
<td>97 Berkelium, Bk</td>
<td>S. G. Thompson, A. Ghiorso and G. T. Seaborg</td>
<td>1949</td>
<td>Bombardment of $^{241}\text{Am}$ with $^2\text{He}$</td>
<td>Berkeley (by analogy with Tb, named after the village of Ytterby)</td>
</tr>
<tr>
<td>98 Californium, Cf</td>
<td>S. G. Thompson, K. Street, A. Ghiorso and G. T. Seaborg</td>
<td>1950</td>
<td>Bombardment of $^{242}\text{Cm}$ with $^2\text{He}$</td>
<td>California (location of the laboratory)</td>
</tr>
<tr>
<td>99 Einsteinium, Es</td>
<td>Workers at Berkeley, Argonne and Los Alamos (USA)</td>
<td>1952</td>
<td>Found in debris of first thermonuclear explosion</td>
<td>Albert Einstein (relativistic relation between mass and energy)</td>
</tr>
<tr>
<td>100 Fermium, Fm</td>
<td>Workers at Berkeley, Argonne and Los Alamos (USA)</td>
<td>1952</td>
<td>Found in debris of first thermonuclear explosion</td>
<td>Enrico Fermi (construction of first self-sustaining nuclear reactor)</td>
</tr>
<tr>
<td>101 Mendelevium, Md</td>
<td>A. Ghiorso, B. H. Harvey, G. R. Choppin, S. G. Thompson and G. T. Seaborg</td>
<td>1955</td>
<td>Bombardment of $^{253}\text{Es}$ with $^2\text{He}$</td>
<td>Dimitri Mendelev (periodic table of the elements)</td>
</tr>
<tr>
<td>102 Nobelium, No(a)</td>
<td>Workers at Dubna, USSR(b)</td>
<td>1965</td>
<td>Bombardment of $^{243}\text{Am}$ with $^{15}\text{N}$ (or $^{238}\text{U}$ with $^{20}\text{Ne}$)</td>
<td>Alfred Nobel (benefactor of science)(a)</td>
</tr>
<tr>
<td>103 Lawrencium, Lr(c)</td>
<td>Workers at Berkeley and at Dubna(d)</td>
<td>1961 – 1971(d)</td>
<td>Bombardment of mixed isotopes of $^{98}\text{Cf}$ with $^{10}\text{B}$, $^{11}\text{B}$; and of $^{243}\text{Am}$ with $^{18}\text{O}$, etc.</td>
<td>Ernest Lawrence (developer of the cyclotron)</td>
</tr>
</tbody>
</table>
only Th and U occur naturally to any useful extent. Indeed, these two elements are far from rare: thorium comprises 8.1 ppm of the earth’s crust, and is almost as abundant as boron, whilst uranium at 2.3 ppm is rather more abundant than tin. The radioactive decay schemes of the Thorium is widely but rather sparsely distributed and its only commercial sources are monazite sands (see p. 1229) and the mineral conglomerates of Ontario.

Separation and preparation of ThO₂ is similar to that of rare earths and is often made in connection to RE separation.
| Thorium series  
(A = 4n) | Neptunium series  
(A = 4n + 1) | Uranium series  
(A = 4n + 2) | Actinium series  
(A = 4n + 3) |
|----------------|----------------|----------------|----------------|
| 232\text{Th}  
(α) \text{1.41x10}^{-10} \text{y} | 241\text{Pu}  
(α) \text{1.43y} | 238\text{U}  
(α) \text{1.468x10}^{3} \text{y} | 235\text{U}  
(α) \text{7.038x10}^{3} \text{y} |
| 228\text{Ra}  
(β) \text{3.76y} | 243\text{Am}  
(β) \text{1.33y} | 234\text{Th}  
(β) \text{24.10d} | 231\text{Th}  
(β) \text{25.52h} |
| 226\text{Ac}  
(β) \text{2.13h} | 237\text{Np}  
(α) \text{6.75h} | 234\text{Pa}  
(β) \text{6.75h} | 234\text{Pa}  
(α) \text{2.25x10}^{4} \text{y} |
| 228\text{Th}  
(α) \text{1.943y} | 233\text{Pa}  
(β) \text{27.0d} | 230\text{U}  
(α) \text{1.592x10}^{3} \text{y} | 227\text{Ac}  
(α) \text{21.77y} |
| 224\text{Ra}  
(α) \text{3.66d} | 233\text{U}  
(β) \text{7.3x10}^{3} \text{y} | 226\text{Ra}  
(α) \text{1.60x10}^{7} \text{y} | 227\text{Th}  
(β) \text{21.8m} |
| 220\text{Rn}  
(α) \text{5.55s} | 231\text{Ra}  
(β) \text{11.44d} | 219\text{Po}  
(α) \text{1.96s} | 223\text{Rn}  
(β) \text{11.44d} |
| 218\text{Po}  
(β+α, 0.15s) \text{0.014%} | 216\text{Bi}  
(β+α, 60.60m) \text{66.3%} | 218\text{Po}  
(β+α, 3.05m) \text{99.96%} | 215\text{Po}  
(β+α, 1.78ms) \text{100%} |
| 216\text{Bi}  
(γ) \text{10.64h} | 216\text{Bi}  
(α) \text{0.30ms} | 216\text{Bi}  
(β) \text{26.8m} | 214\text{Bi}  
(γ) \text{19.7m} |
| 214\text{Bi}  
(β) \text{26.8m} | 216\text{Bi}  
(α) \text{32.3ms} | 214\text{Bi}  
(β) \text{36.1m} | 211\text{Bi}  
(γ) \text{19.7m} |
| 210\text{Bi}  
(β) \text{1.30m} | 210\text{Bi}  
(α) \text{0.516s} | 210\text{Bi}  
(β) \text{123y} | 208\text{Pb}  
(β) \text{4.77m} |
| 210\text{Bi}  
(β) \text{1.30m} | 210\text{Pb}  
(β) \text{123y} | 210\text{Pb}  
(β) \text{1.25h} | 209\text{Pb}  
(β) \text{1.30m} |
| 209\text{Bi}  
(β) \text{3.05m} | 209\text{Bi}  
(β) \text{2.7m} | 208\text{Pb}  
(β) \text{10.7d} | 208\text{Pb}  
(β) \text{1.30m} |
| 208\text{Pb}  
(α) \text{4.20m} | 208\text{Pb}  
(α) \text{138.38d} | 208\text{Pb}  
(α) \text{138.38d} | 205\text{Pb}  
(β) \text{4.20m} |

The radioactive decay series.
Uranium production depends in detail on the nature of the ore involved but, after crushing and concentrating by conventional physical means, the ore is usually roasted and leached with sulfuric acid in the presence of an oxidizing agent such as MnO₂ or NaClO₃ to ensure conversion of all uranium to UO₂²⁺. In a typical process the uranium is concentrated as a sulfato complex on an anion exchange resin from which it is eluted with strong HNO₃ and further purified by solvent extraction into tributyl phosphate (TBP) in either kerosene or hexane. The uranium is then stripped from the organic phase to give an aqueous sulfate solution from which so-called “yellow cake” is precipitated* by addition of ammonia. This is converted to UO₃ by heating at 300°C, and then to UO₂ by reducing in H₂ at 700°C. Conversion to the metal is generally effected by reduction of UF₄ with Mg at 700°C.

Uranium is almost entirely used for nuclear fuel

70 000 tons of U₃O₈ produced in 2013.
Kazakhstan 31 %
Canada 13 %
Australia  9 %
Niger 6.5 %
Namibia 6 %
Russia 4.4 %
Uzbekistan 3.4 %
USA 2.6 %
China 2.1 %
Malawi 1.7 %
Nuclear reactors and atomic energy

In the process of nuclear fission a large nucleus splits into two highly energetic smaller nuclei and a number of neutrons; if there are sufficient neutrons and they have the correct energy, they can induce fission of further nuclei, so creating a self-propagating chain reaction. The kinetic energy of the main fragments is rapidly converted to heat as they collide with neighbouring atoms, the amount being of the order of $10^6$ times that produced by chemically burning the same mass of combustible material such as coal.

In practical terms, the only naturally occurring fissile nucleus is $^{235}_{92}$U (0.72% abundance):

$$^{235}_{92}U + ^1_0n \rightarrow 2 \text{ fragments} + x^1_0n \quad (x = 2-3)$$

Fission produces fast neutrons which are inefficient for further fission reactions. In order to get chain reaction the neutrons must be slowed down and the $^{235}$U content in the fuel enriched to 2-3 % content.
Early reactors used uranium in metallic form but this has been superseded by $^{235}\text{U}$ which is chemically less reactive and has a higher melting point. $\text{UC}_2$ is also sometimes used but is reactive towards $\text{O}_2$.

In addition to $^{235}\text{U}$, which occurs naturally, two other fissile nuclei are available artificially. These are $^{239}\text{Pu}$ and $^{233}\text{U}$ which are obtained from $^{238}\text{U}$ and $^{232}\text{Th}$ respectively:

\[
^{238}\text{U} + ^1\text{n} \longrightarrow ^{239}\text{U} \quad \longrightarrow ^{239}\text{Np} \quad \longrightarrow ^{239}\text{Pu} \quad \longrightarrow ^{233}\text{Pa} \quad \longrightarrow ^{233}\text{U}
\]

\[
^{232}\text{Th} + ^1\text{n} \longrightarrow ^{233}\text{Th} \quad \longrightarrow ^{233}\text{Pa} \quad \longrightarrow ^{233}\text{U}
\]

$^{239}\text{Pu}$ is therefore produced to some extent in all currently operating reactors because they contain $^{238}\text{U}$, and this contributes to the reactor efficiency. More significantly, it
Fuel enrichment. All practicable enrichment processes require the uranium to be in the form of a gas. UF₆, which readily sublimes (p. 1269), is universally used and, because fluorine occurs in nature only as a single isotope, the compound has the advantage that separation depends solely on the isotopes of uranium.

Enrichment:
- By diffusion through membranes (old method)
- With centrifuges (1000 rps) – many times in cascade
- Laser ionisation separation

Neutrons slowed by moderators
For cooling many methods (water)
Recycling of the fuel is important. It is one of the most demanding processes in chemical industry.
Properties of metals are quite similar to those of lanthanides:

- Silver white, reactive (tarnish in air moisture)
- Tolerate acids better than expected (alkalis too). Concentrated HNO$_3$ passivates (adding F$^-$ dissolves)
- React with most non-metals if heated
- In boiling water H$_2$ is liberated
- Metal properties largely studied only for U and Th

<table>
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<tr>
<th>Property</th>
<th>Th</th>
<th>Pa</th>
<th>U</th>
<th>Np</th>
<th>Pa</th>
<th>Am</th>
<th>Cm</th>
<th>Bk</th>
<th>Cf</th>
<th>Es</th>
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<th>Md</th>
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<td>Number of naturally occurring isotopes</td>
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<td>Mass number</td>
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<td>Half-life (a)</td>
<td>1.40 × 10$^6$</td>
<td>3.25 × 10$^7$</td>
<td>4.47 × 10$^7$</td>
<td>2.14 × 10$^7$</td>
<td>2.41 × 10$^7$</td>
<td>1.81 × 10$^7$</td>
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<td>520 d</td>
<td>6.5 y</td>
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<td>100.5 d</td>
<td>78 min</td>
<td>58 min</td>
<td>3.6 h</td>
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<td>Relative nuclidic mass</td>
<td>232 0390</td>
<td>231 0399</td>
<td>238 0289</td>
<td>237 0462</td>
<td>239 0522</td>
<td>241 0568</td>
<td>244 0627</td>
<td>249 0750</td>
<td>252 0816</td>
<td>252 0830</td>
<td>257 0951</td>
<td>256 0941</td>
<td>293 1011</td>
<td>262 1100</td>
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<td>Electronic configuration, [Rn]</td>
<td>[Ar]</td>
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<td>Metal radius (CN12)/pm</td>
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<td>163</td>
<td>156</td>
<td>153</td>
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<td>173</td>
<td>174</td>
<td>170</td>
<td>186 ± 2</td>
<td>186 ± 2</td>
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<td>Ionic radius (CN6)/pm</td>
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<tr>
<td>E$^\prime$(MO$_2$)$^+/$(MO$_3$)$^+$/V</td>
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<td>E$^\prime$(MO$_2$)$^+/$(MO$_3$)$^+$/V</td>
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</table>
Figure 31.4  Metal and ionic radii of Ac and the actinides.
First, most stable when all valence electrons are removed. After half-filled 5-f orbital +3 oxidation starts to dominate.
MO$_2^{n+}$ species common
With uranium uranyl (UO$_2^{2+}$) compounds are common.

Figure 31.5 Volt-equivalent versus oxidation state for actinide ions.
### Table 31.4 Oxidation states and stereochemistries of compounds of the actinides

“An” is used as a general symbol for the actinide elements.

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Coordination number</th>
<th>Stereochemistry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>16</td>
<td>See Figs. 19.31 and 31.10</td>
<td><img src="An(%CE%B7%5E5-C_8H_8)_2" alt="Equation" /> (An = Th → Pu), [Li(η^5-C_8H_4Ph)_2]</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>Octahedral</td>
<td><img src="AnCl_3" alt="Equation" /> (An = Np, Am, Bk)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Bicapped trigonal prismatic</td>
<td><img src="AnCl_3" alt="Equation" /> (X = Br, An = Pu → Bk; X = I, An = Pa → Pu)</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Tricapped trigonal prismatic</td>
<td><img src="AnCl_3" alt="Equation" /> (An = U → Cm)</td>
</tr>
<tr>
<td>4</td>
<td>See p. 1278</td>
<td>Complex</td>
<td><img src="U(NPh_2)_4" alt="Equation" /></td>
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<tr>
<td></td>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td><img src="U_2(NEt_2)_8" alt="Equation" /></td>
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<tr>
<td></td>
<td>6</td>
<td>Octahedral</td>
<td><img src="AnX_6" alt="Equation" />_2(^{2-}) (An = U, Np, Pu; X = Cl, Br)</td>
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<tr>
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<td>7</td>
<td>Pentagonal bipyramidal</td>
<td><img src="UBr_4" alt="Equation" /></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Cubic</td>
<td><img src="An(NCS)_3" alt="Equation" />_4(^{2-}) (An = Th → Pu)</td>
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<tr>
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<td>9</td>
<td>Dodecahedral</td>
<td><img src="Th(C_2O_4)_4" alt="Equation" />_4(^{4-}), <img src="An(S_2CNEt_2)_4" alt="Equation" /> (An = Th, U, Np, Pu)</td>
</tr>
<tr>
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<td>10</td>
<td>Square antiprismatic</td>
<td><img src="An(acac)_4" alt="Equation" /> (An = Th, U, Np, Pu)</td>
</tr>
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<td>11</td>
<td>Tricapped trigonal prismatic</td>
<td><img src="NH_4" alt="Equation" />_3[ThF_7]</td>
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<tr>
<td></td>
<td>12</td>
<td>Capped square antiprismatic</td>
<td><img src="K_4%5BTh(C_2O_4)_4%5D.4H_2O" alt="Equation" /></td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>Bicapped square antiprismatic</td>
<td>![Equation](K_4[Th(NO_3)_4(OPPh_3)_2]^{(a)}</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Icosahedral</td>
<td><img src="Th(NO_3)_6" alt="Equation" />_2(^{2-})(^{(a)})</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>Bicapped hexagonal antiprismatic</td>
<td><img src="U%5BBH_4%5D_4" alt="Equation" /></td>
</tr>
<tr>
<td>5</td>
<td>See Fig. 31.8a</td>
<td>Octahedral</td>
<td><img src="Cs%5BAnF_6%5D" alt="Equation" /> (An = U, Np, Pu)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Pentagonal bipyramidal</td>
<td><img src="Na_3%5BAnF_6%5D" alt="Equation" /> (An = Pa, U, Np)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Cubic</td>
<td><img src="M_2%5BPaF_7%5D" alt="Equation" /> (M = NH_4, K, Rb, Cs)</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>Octahedral</td>
<td><img src="AnF_6" alt="Equation" /> (An = U, Np, Pu), UCl_6, Cs_2[UO_2X_4]^{(b)} (X = Cl, Br)</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Pentagonal bipyramidal</td>
<td><img src="UO_2(S_2CNEt_2)_2(ONMe_3)" alt="Equation" />^{(b)}</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Hexagonal bipyramidal</td>
<td><img src="UO_2(NO_3)_2(H_2O)_2" alt="Equation" />^{(b)}</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Octahedral</td>
<td><img src="Li_5%5BAnO_6%5D" alt="Equation" /> (An = Np, Pu)</td>
</tr>
</tbody>
</table>
Actinide oxides are refractory materials (tolerate high-temperatures). Oxides are basic in nature. Dissolve best in HNO$_3$. Hydroxides precipitate as colloids. Water solutions of actinoids yield AnO$_2$(OH)$_2$. Mixed oxides with M(I), M(II) cations with different stoichiometry.

![Table 31.5 Oxides of the Actinide Elements\(^{(a)}\)](image)

The most stable oxide of each element is printed in **bold**.

<table>
<thead>
<tr>
<th>Formal oxidation state of metal</th>
<th>Th</th>
<th>Pa</th>
<th>U</th>
<th>Np</th>
<th>Pu</th>
<th>Am</th>
<th>Cm</th>
<th>Bk</th>
<th>Cf</th>
<th>Es</th>
</tr>
</thead>
<tbody>
<tr>
<td>+6</td>
<td></td>
<td></td>
<td>UO$_3$</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>o-y</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>U$_3$O$_8$</td>
<td>dark g</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+5</td>
<td></td>
<td>Pa$_2$O$_5$</td>
<td>white</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>PaO$_2$</td>
<td>black</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>+4</td>
<td>ThO$_2$</td>
<td>white</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>PaO$_2$</td>
<td>black</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>+3</td>
<td></td>
<td></td>
<td>UO$_2$</td>
<td>dark br</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NpO$_2$</td>
<td>br-g</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>PuO$_2$</td>
<td>y-br</td>
<td>AmO$_2$</td>
<td>black</td>
<td>CmO$_2$</td>
<td>black</td>
<td>BkO$_2$</td>
<td>black</td>
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</tbody>
</table>

\(^{(a)}\)br = brown; g = green; o = orange; r = red; y = yellow.

\(^{(b)}\)This is the only known oxide of Es. It is expected to be the most stable for this actinide but investigation of the Es/O system is hampered not only by low availability but also by the high $\alpha$-activity ($t_{\frac{1}{2}} = 20.5$ days) which causes crystals to disintegrate. Es$_2$O$_3$ was characterized by electron diffraction using microgram samples measuring only about 0.03 $\mu$m on edge.
Hexahalides are molecular compounds, extremely sensitive to water: $\text{AnX}_6 + \text{H}_2\text{O} \rightarrow \text{AnO}_2\text{X}_2 + 4\text{HX}$

Pentahalides for Pa, U, Np. Polymeric, pentagonal bipyramid, 2 halides form bridge.

Tetrahalides common. Fluoride is inert, others hygroscopic. 8-coordination.

Trihalides for all An. Very similar to corresponding Ln halides.

Oxoihalides also known.
Magnetic and spectroscopic properties

As the actinides are a second f series it is natural to expect similarities with the lanthanides in their magnetic and spectroscopic properties. However, while previous treatments of the lanthanides (p. 1242) provide a useful starting point in discussing the actinides, important differences are to be noted. Spin–orbit coupling is again strong (2000–4000 cm⁻¹) but, because of the greater exposure of the 5f electrons, crystal-field splittings are now of comparable magnitude and J is no longer such a good quantum number. Furthermore, as already mentioned (p. 1266), the energy levels of the 5f and 6d orbitals are sufficiently close for the lighter actinides at least, to render the 6d orbitals accessible. As a result, rigorous treatments of electronic properties must consider each actinide compound individually. They must allow for the mixing of "J levels" obtained from Russell–Saunders coupling and for the population of thermally accessible excited levels. Accordingly, the expression \( \mu_e = g\sqrt{J(J + 1)} \) is less applicable than for the lanthanides: the values of magnetic moment obtained at room temperature roughly parallel those obtained for compounds of corresponding lanthanides (see Table 30.6), but they are usually appreciably lower and are much more temperature-dependent.
The electronic spectra of actinide compounds arise from three types of electronic transition:

(i) \( f \rightarrow f \) transitions (see p. 1243). These are orbitally forbidden, but the selection rule is partially relaxed by the action of the crystal field in distorting the symmetry of the metal ion. Because the field is stronger than for the lanthanides, the bands are more intense by about a factor of 10 and, though still narrow, are about twice as broad and are more complex than those of the lanthanides. They are observed in the visible and ultraviolet regions and produce the colours of aqueous solutions of simple actinide salts as given in Table 31.3.

(ii) \( 5f \rightarrow 6d \) transitions. These are orbitally allowed and give rise to bands which are therefore much more intense than those of type (i) and are usually rather broader. They occur at lower energies than do the \( 4f \rightarrow 5d \) transitions of the lanthanides but are still normally confined to the ultraviolet region and do not affect the colour of the ion.

(iii) Metal → ligand charge transfer. These again are fully allowed transitions and produce broad, intense absorptions usually found in the ultraviolet but sometimes trailing into the visible region. They produce the intense colours which characterize many actinide complexes, especially those involving the actinide in a high oxidation state with readily oxidizable ligands.

Lanthanides do not show \( M \rightarrow L \) electronic transitions.
Metal complexes

All oxidation states possible. +VI important and "actinyl" compounds dominate. An-O bond strength decreases in series U>Np>Pl>Am.
**Oxidation state V**

In aqueous solution the $\text{AnO}_2^+$ ions ($\text{An} = \text{Pa} \rightarrow \text{Am}$) may be formed, at least in the absence of strongly coordinating ligands. They are linear cations like $\text{AnO}_2^{2+}$ but are less persistent and, indeed, it is probable that $\text{PaO}_2^+$ should be formulated as $[\text{PaO(OH)}_2]^+$ and $[\text{PaO(OH)}]^2+$. Hydrolysis is extensive in aqueous solutions of $\text{Pa}^{\text{V}}$ and colloidal hydroxo species are formed which readily lead to precipitation of $\text{Pa}_2\text{O}_5.\text{nH}_2\text{O}$. $\text{NpO}_2^+$ in aqueous $\text{HClO}_4$ is stable but $\text{UO}_2^+$, $\text{PuO}_2^+$ and $\text{AmO}_2^+$ are unstable to disproportionation:

$$2\text{UO}_2^+ \leftrightarrow \text{U}^{\text{IV}} + \text{UO}_2^{2+} \quad \text{(very rapid except in the range pH 2–4)}$$

$$2\text{PuO}_2^+ \leftrightarrow \text{Pu}^{\text{IV}} + \text{PuO}_2^{2+}$$

and then $\text{PuO}_2^+ + \text{Pu}^{\text{IV}} \leftrightarrow \text{Pu}^{\text{III}} + \text{PuO}_2^{2+}$.†

Likewise:

$$3\text{AmO}_2^+ \leftrightarrow \text{Am}^{\text{III}} + 2\text{AmO}_2^{2+}$$

Though the low charge on $\text{AnO}_2^+$ ions precludes the formation of very stable complexes, and disproportionation into $\text{An}^{\text{IV}}$ and $\text{An}^{\text{VI}}$ species is common, a number of complexes of $\text{NpO}_2^+$ have been prepared,$^{(34)}$ several containing the pentagonal bipyramidal $[\text{NpO}_2(\text{SO}_4)_2\text{L}]$ unit. In other cases, strongly coordinating ligands are able to replace the oxygen atoms of the $\text{AnO}_2^+$ ions and so inhibit disproportionation where this might otherwise occur. $\text{F}^-$ is notable in this respect and complex ions, $\text{AnF}_6^-$ ($\text{An} = \text{Pa, U, Np, Pu}$), $\text{PaF}_7^{2-}$ and $\text{PaF}_8^{3-}$ can be precipitated from aqueous HF solutions. However, in nonaqueous
Oxidation state IV

This is the only important oxidation state for Th, and is one of the two for which U is stable in aqueous solution; it is moderately stable for Pa and Np also. In water Pu^{IV}, like Pu^{V}, disproportionates into a mixture of oxidation states III, IV, V and VI, while Am^{IV} not only disproportionates into Am^{III} + Am^{V}O_{2}^{2+} but also (like the strongly oxidizing Cm^{IV}) undergoes rapid self-reduction due to its α-radioactivity. As a result, aqueous Am^{IV} and Cm^{IV} require stabilization with high concentrations of F^- ion. Berkelium(IV), though easily reduced, clearly has an enhanced stability, presumably due to its f^7 configuration, and the only other +4 ion is Cf^{IV}, found in the solids CfF_{4} and CfO_{2}.

The isolation of An^{IV} salts with oxoanions is limited by hydrolysis and redox compatibility. Thus, with the possible exception of Pu(CO_{3})_{2}, carbonate ions furnish only basic carbonates or carbonato complexes such as [An(CO_{3})_{5}]^{6-} (An = Th, U, Pu). Stable tetranitrates are isolable only for Th and Pu, but Th(NO_{3})_{4}.5H_{2}O is the most common salt of Th and is notable as the first confirmed example of 11-coordination (Fig. 31.8(a)). Pu(NO_{3})_{4}.5H_{2}O

Anionic complexes [An(NO_{3})_{6}]^{2-} (An = Th, U, Np, Pu) are also obtained, that of Th, and probably the others, having bidentate NO_{3}^{-} ions forming a slightly distorted icosahedron similar to that of the Ce^{IV} analogue (see Fig. 30.5a). Th(ClO_{4})_{4}.4H_{2}O is readily obtained from aqueous solutions but attempts to prepare the U^{IV} salt have produced a green explosive solid of uncertain composition. Hydrated sulfates are known for Th, U, Np and Pu. That of Np is of

The actinides provide a wider range of complexes in their +4 oxidation state than in any other, and these display the usual characteristics of actinide complexes, namely high coordination numbers and varied geometry. Complexes with halides and with O-donor chelating ligands are particularly numerous. The main fluoro-complexes are of the types [AnF_{5}]^{-}, [AnF_{6}]^{2-}, [AnF_{7}]^{3-}, [AnF_{8}]^{4-} and [An_{6}F_{31}]^{7-} which are nearly all known for An = Th →
**Oxidation state III**

This is the only oxidation state which, with the possible exception of Pa, is displayed by all actinides. From U onwards, its resistance to oxidation in aqueous solution increases progressively with increase in atomic number and it becomes the most stable oxidation state for Am and subsequent actinides (except No for which the \(f^{14}\) configuration confers greater stability on the +2 state).

**Oxidation state II**

This state is found for the six elements Am and Cf \(\rightarrow\) No, though in aqueous solution only for Fm, Md and No. However, for No, alone amongst all the f-series elements, it is the normal oxidation state in aqueous solution. The greater stabilization of the +2 state at the end of the actinides as compared to that at the end of the lanthanides which this implies, has been taken\(^{40}\) to indicate a greater separation between the 5f and 6d than between the 4f and 5d orbitals at the ends of the two series. This is the reverse of the situation found at the beginnings of the series (p. 1266).
Organometallic chemistry

The cyclopentadienyls are of the three main types: (a) \([\text{An}^{\text{III}}(\text{C}_5\text{H}_5)_3]\), (b) \([\text{An}^{\text{IV}}(\eta^5-\text{C}_5\text{H}_5)_4]\) and (c) derivatives of the type \([\text{An}^{\text{IV}}(\eta^5-\text{C}_5\text{H}_5)_3\text{X}]\) where \(\text{X}\) is a halogen atom, an alkyl or alkoxy group, or BH₄.

(a) \([\text{An}^{\text{III}}(\text{C}_5\text{H}_5)_3]\) (An = Th → Cf): the uranium compound is prepared directly from UCl₃ and K(C₅H₅) but those of the heavier actinides are best made by the reaction:

\[
2\text{AnCl}_3 + 3\text{Be(C}_5\text{H}_5)_2 \xrightarrow{65^\circ\text{C}} 2\text{An(C}_5\text{H}_5)_3 + 3\text{BeCl}_2
\]

Complete structural data are sparse but X-ray diffraction patterns suggest that both \(\eta^5\) and \(\eta^1\) bonding modes are involved (cf. Sm(C₅H₅)₃ p. 1248). In [Th^{III}(\eta^5-\text{C}_5\text{H}_5(\text{SiMe}_3)_2)_3] the centres of three rings form a trigonal plane around the Th atom.\(^{43}\) The spectroscopic properties of this blue paramagnetic compound imply a 6\(d^1\) rather than 5\(f^1\) configuration.\(^{44}\)

(b) \([\text{An}^{\text{IV}}(\text{C}_5\text{H}_5)_4]\) (An = Th → Np): the Pa compound is prepared by treating PaCl₄ with Be(C₅H₅)₂ but the general method of preparation is:

\[
\text{AnCl}_4 + 4\text{K(C}_5\text{H}_5) \xrightarrow{\text{reflux in C}_6\text{H}_6} \text{[An(C}_5\text{H}_5)_4] + 4\text{KCl}
\]

\([\text{M(C}_5\text{H}_5)_4]\) (M = Th, U) contain four identical \(\eta^5\) rings arranged tetrahedrally around the metal atom (Fig. 31.9). The corresponding compounds of Pa and Np are probably the same since all four compounds have very similar nmr and IR spectra.

![Figure 31.9](image_url)

Figure 31.9 Structure of \([\text{An}(\eta^5-\text{C}_5\text{H}_5)_4]\) showing the tetrahedral arrangement of the four rings around the metal atom.

(c) Halide derivatives: the most plentiful are of the type \([\text{An}^{\text{IV}}(\text{C}_5\text{H}_5)_3\text{X}]\) (An = Th, Pa, U, Np); they can be prepared by the general reaction:

\[
\text{AnX}_4 + 3\text{M}^1(\text{C}_5\text{H}_5) \longrightarrow [\text{An(C}_5\text{H}_5)_3\text{X}] + 3\text{M}^1\text{X}
\]