The Actinide series contains elements with atomic numbers 89 to 103 and is the third group in the periodic table. The series is the row below the Lanthanide series, which is located underneath the main body of the periodic table. Lanthanide and Actinide Series are both referred to as Rare Earth Metals. These elements all have a high diversity in oxidation numbers and all are radioactive. The most common and known element is Uranium, which is used as nuclear fuel when its converted into plutonium, through a nuclear reaction.

**History of the Actinides**

The first actinides to be discovered were Uranium by Klaproth in 1789 and Thorium by Berezelius in 1829, but most of the Actinides were man-made products of the 20th century. Actinium and Protactinium are found in small portions in nature, as decay products of 253-Uranium and 238-Uranium. Microscopic amounts of Plutonium are made by neutron capture by Uranium, and yet occur naturally. Monazite is the principle Thorium ore. It is a phosphate ore that contains great amounts of Lanthanides in it. The main Uranium ore is U₃O₈ and is known as pitchblende, because it occurs in black, pitch-like masses. An example of pitchblende is located in the picture below. All elements past Uranium are man-made. Actinides require special handling, because many of them are radioactive and/or unstable. The radiation in actinides plays a large role in the chemistry and arrangement of particles in crystals.

*This is a picture of U₃O₈, a uranium, pitchblende ore, by Geomartin.*

**Common Properties**

- All are radioactive due to instability.
- Majority synthetically made by particle accelerators creating nuclear reactions and short lasting.
- All are unstable and reactive due to atomic number above 83 (nuclear stability).
- All have a silvery or silvery-white luster in metallic form.
- All have the ability to form stable complexes with ligands, such as chloride, sulfate, carbonate and acetate.
- Many of the actinides occur in nature as sea water or minerals.
- They have the ability to undergo nuclear reactions.
• The emission of radioactivity, toxicity, pyrophoricity, and nuclear criticality are properties that make them hazardous to handle.
  ◦ **Emission of Radioactivity**: The types of radiation the elements possess are alpha, beta, gamma, as well as when neutrons are produced by spontaneous fissions or boron, beryllium, and fluorine react with alpha-particles.
  ◦ **Toxicity**: Because of their radioactive and heavy metal characteristics, they are considered toxic elements.
  ◦ **Pyrophoricity**: Many actinide metals, hydrides, carbides, alloys and other compounds may ignite at room temperature in a finely divided state, which would result from spontaneous combustion fires and spreading of radioactive contaminates.
  ◦ **Nuclear Criticality**: If fissionable materials are combined, a chain reaction could occur resulting in lethal doses of radioactivity, but it depends on chemical form, isotopic composition, geometry, size of surroundings, etc.

• The interaction of Actinides when radioactive with different types of phosphors will produce pulses of light.

---

**Table [PageIndex(1)]: Actinide Properties**

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Symbol</th>
<th>Name</th>
<th>Atomic Mass (g/mol)</th>
<th>Electron Configuration</th>
<th>Oxidation States</th>
<th>Year Discovered</th>
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<tbody>
<tr>
<td>89</td>
<td>Ac</td>
<td>Actinium</td>
<td>227</td>
<td>[Rn] 6d²7s²</td>
<td>+3</td>
<td>1899</td>
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<tr>
<td>90</td>
<td>Th</td>
<td>Thorium</td>
<td>232.04</td>
<td>[Rn] 6d²7s²</td>
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<td>91</td>
<td>Pa</td>
<td>Protactinium</td>
<td>231.04</td>
<td>[Rn] 5f²6d¹7s²</td>
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<td>U</td>
<td>Uranium</td>
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<td>[Rn] 5f³6d¹7s²</td>
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<tr>
<td>93</td>
<td>Np</td>
<td>Neptunium</td>
<td>237</td>
<td>[Rn] 5f⁴6d¹7s²</td>
<td>+3,+4,+5,+6,+7</td>
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<tr>
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<td>Pu</td>
<td>Plutonium</td>
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<td>Am</td>
<td>Americium</td>
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<tr>
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<td>Curium</td>
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<tr>
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<td>Berkelium</td>
<td>247</td>
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<tr>
<td>98</td>
<td>Cf</td>
<td>Californium</td>
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<tr>
<td>99</td>
<td>Es</td>
<td>Einsteinium</td>
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<td>100</td>
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<td>Fermium</td>
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<tr>
<td>101</td>
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<td>Mendelevium</td>
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<td>Oxidation States</td>
<td>Year Discovered</td>
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<tr>
<td>---------------</td>
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<td>------------------------</td>
<td>------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>102</td>
<td>No</td>
<td>Nobelium</td>
<td>[259]</td>
<td>[Rn] 5f^{14}7s^2</td>
<td>+2,+3</td>
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<tr>
<td>103</td>
<td>Lr</td>
<td>Lawrencium</td>
<td>[262]</td>
<td>[Rn] 5f^{14}6d^{1}7s^2</td>
<td>+3</td>
<td>1961</td>
</tr>
</tbody>
</table>

- [#]-mass number of the longest living isotope is given when the element has no stable nuclotides.
- (?)-oxidation state is unconfirmed

Actinides have been crucial in understanding nuclear chemistry and have provided valuable usage today, such as nuclear power. These examples illustrate their importance in understanding key concepts in nuclear chemistry and related topics.

### Transition Metal

Actinides are in the f-block of the periodic table. The electron configuration of uranium is [Rn] 5f^3 6d^1 7s^2. The reason for this arrangement unlike other conventional electron configurations such as Na with configuration of [Ne]3s^2 is due to the fact that some orbitals fill in faster than others and explains why Actinides are transition metals. (see transition metals)

The electron configurations of the actinides are due to the following:

- The energy in the 6d orbitals is lower in energy than in the 5f orbitals.
- They fill 5f orbital, 6d orbital, then 7s orbital.
- The 5f orbitals are not shielded by the filled 6s and 6p subshells.
- There is a small energy gap between the 5f^n 7s^2 and 5f^{n-1} 6d 7s^2 configurations.
- The 5f orbitals do not shield each other from the nucleus effectively.
- The energies of the 5f orbital drop rapidly with increasing atomic number.

### Chemistry

- **Actinium**
  - Its chemistry is dominated by (+3) O. S.
  - Its compounds are colorless.
  - There are 29 known isotopes.
  - It does not have absorption in the UV visible region between 400-1000nm.
  - $^{227}$Ac is strongly radioactive and so are its decay components.
  - Actinium metal is silvery solid; obtained by reduction of oxide, fluoride or chloride w/ Group 1 metals; and oxidized rapidly in moist air.
  - It forms insoluble fluoride and oxalate ($\text{Ac}_2(\text{C}_2\text{O}_4)_3*10\text{H}_2\text{O}$) compounds
• **Thorium**
  ◦ It exhibits the +4 O.S. exclusively.
  ◦ The chemistry in the +2 and +3 O.S. is restricted to iodides like ThI$_2$ and cyclopentadienyl Th(C$_5$H$_5$)$_3$.
  ◦ It has wide coordination chemistry with oxygen donor ligands.
  ◦ Thorium metal is bright and silvery-white and tarnishes to a dull black color when exposed to air. It is soft enough to be scratched with a knife and melts at 1750°. It slowly dissolves in dilute with hydrogen evolution and can be pyrophoric as a powder.

• **Protactinium**
  ◦ It has been in existence longer than any other actinide.
  ◦ $^{231}$Pa has a half-life of $3.28 \times 10^{14}$ which allows it to make chemical study easy for it.
  ◦ It has α-emission, so it has appropriate radiochemical precautions.
  ◦ The Pa metal is malleable, ductile, silvery, and has a melting point of about 1565°C. It is also a superconductor.

• **Uranium**
  ◦ Many compounds exist between the O.S. of +3 to +6.
  ◦ The main O.S. are +4 and +6.
  ◦ Stability of O.S.
    ▪ $^{3+}$ reduces to hydrogen
    ▪ $^{4+}$ stable in aqueous solution in the absence of air
    ▪ $^{5+}$ disproportionates rapidly into a mixture of $^{4+}$ and $^{6+}$ in aqueous solutions
    ▪ $^{6+}$ stable in aqueous solutions
  ◦ When pure it has a silvery appearance.
  ◦ When attacked by air, yellow film then black coating develops, it is a mix of oxide and nitride.
  ◦ Powder metal is pyrophoric in air.
  ◦ Reacts readily with hot water to prevent substances from coming into contact in nuclear reactors

• **Neptunium**
  ◦ It was the first transuranium element to be discovered in 1940.
  ◦ There are 15 known isotopes, only $^{237}$Np, w/ half-life of $2.14 \times 10^6$ years, is useful for chemical experiments.
  ◦ It exhibits O.S. of +3 to +7 in compounds.
  ◦ It is a silvery metal, with a melting point of 637°C and a boiling point of 4174°C.
  ◦ It has surface oxidation when exposed to air.
  ◦ It is converted to NpO$_2$ at high temperatures.

• **Plutonium**
  ◦ There are 15 known isotopes.
    ▪ The masses range from 232 to 246.
    ▪ The most important isotope is $^{239}$Pu because it is fissionable and has a half-life of 24,100 years, which makes it easy for chemists to study.
  ◦ It exhibits O.S. from +3 to +7.
• The +3 and +4 O.S. are the most important, but compounds of the ions are well defined.
• Pu$^{+7}$ only exists under very alkaline conditions.
  ◦ It has 6 allotropic metal forms, which makes it unusual.
  ◦ They can form at normal pressure between room temperature and its melting point, 640°C.
  ◦ It is dense, silvery and a reactive metal; more reactive than uranium or neptunium.
  ◦ When attacked by air, it forms a green-gray oxide coating.
  ◦ It reacts slowly with cold water, faster with dilute H$_2$SO$_4$, and dissolves quickly in dilute hydrochloric acid or hydrobromic acid.

• **Americium**
  ◦ It has 12 known isotopes.
  ◦ It was first made in 1944-1945 by Seaborg and his coworkers, where they decayed $^{239}$Pu and $^{241}$Pu to $^{241}$Am, which has a half-life of 433 years.
  ◦ $^{241}$Am and $^{243}$Am, which has a half-life of 7380 years are the most important isotopes, because their half-lives allow scientists to study their characteristics.
  ◦ The metal is a silvery, ductile and very malleable.
  ◦ It tarnishes in air slowly and dissolves in dilute hydrochloric acid quickly.
  ◦ It reacts with heating with oxygen, halogens, and other nonmetals

• **Later Actinides (Cm, Bk, Cf, Es, Fm, Md, No, and Lr)**
  ◦ Their chemistry is of mostly the M$^{+3}$ state.
  ◦ They all form binary compounds, such as trihalides.
  ◦ Curium, berkelium, and californium have the following chemistry:
    • Oxidized by air to the oxide
    • Electropositive
    • Reacts with hydrogen on warming to form hydrides
    • Yields compounds on warming with group 5 and group 6 non-metals

---

**Solubility and Precipitation**

Knowing about the solubility and precipitations of actinides, help chemists understand their properties better. Not all Actinides have the same properties when it comes solubility and precipitation, but most of the Actinides have similar traits and characteristics.

The fluorides, hydroxides and oxalates of actinides have low solubilities. The lighter trivalent, having a valence of three electrons, are unstable in aqueous solutions, such as transplutonium elements. The actinides of light weight have a higher valence; for example, oxidation states of 4, 5 and 6 where they are more stable; and they form compounds with low solubility. Trivalent Actinides can be separated from slightly acidic solutions as phosphates, mildly acidic solutions as oxalates, strongly acidic solutions as fluorides, and from basic solutions as hydroxides or hydrous oxides.

Hydrogen peroxide precipitates Pu$^{+4}$, Th$^{+4}$, Ce$^{+4}$, U$^{+4}$, Np$^{+4}$ and Pa$^{+4}$. Pu$^{+4}$, Th$^{+4}$, Np$^{+4}$, UO$^{2+}$ and all trivalent actinides are precipitated by carbonate-free ammonium hydroxide. The solubility of Actinide hydroxides or hydrous oxides in strong...
ammonium carbonate solutions allow the separation or Uranium and Thorium from other members of the Ammonium hydroxide group, such as Fe, Ti, Al and other rare earth metals. Thorium can be precipitated from ammonia with aluminum or from aluminum as a fluoride or oxalate. Uranium is precipitated with hydrogen sulfide, unless a complexing agent is present, such as Tartaric acid (C_{4}H_{6}O_{6}), and can be precipitated with Ammonium sulfide, unless Ammonium carbonate is present.

**Halides**

A majority of actinides form halides with halogens at specific temperatures and trihalides are the most well known halides. The following are examples of Actinide compounds forming with halide compound creating actinide halide compounds:

\[
\text{\underbrace{\text{Ac(OH)3 + 3HF ->[700°C] AcF3 + 3H2O}}}_{\text{Fluorides}}
\]

\[
\text{\underbrace{\text{Ac2O3 + 6NH4Cl ->[250°C] 2AcCl3 + 6NH3 + 3H2O}}}_{\text{Chlorides}}
\]

\[
\text{\underbrace{\text{Ac2O3 + 2AlBr3 ->[750°C] 2AcBr3 + Al2O3 }}}_{\text{Bromides}}
\]

\[
\text{\underbrace{\text{Th + 2I2->[400°C] ThI4 }}}_{\text{Iodides}}
\]

The halides are very important binary compounds, sometimes the most important. Although they may have radioactivity that causes problems, they are useful to study to understand the trends in the Actinide series. Below are some halide characteristics of the actinide series from Actinium to Einsteinium.

- **Actinium:**
  - forms halides in the oxidation state of +3 only.

- **Thorium:**
  - forms in the 2, 3, and 4 oxidation states.
  - exists in black and gold forms.
  - has high conductivity.
  - contains free electrons.
  - has all whites are solids.
  - forms many complexes with neutral donors.
  - has an eight coordination number (dodecahedron, sq antiprism).

- **Protactinium:**
  - forms many different types of halides and several oxyhalides.
  - chlorides (PaCl$_5$) are yellow-green, bromides (PaBr$_4$) are orange-red, fluorides (PaF$_4$) are brown, and iodides (PaI$_3$) are dark brown.
  - has six coordinate (dimeric), eight coordinate (dodecahedral and square antiprismatic), seven coordinate, and nine coordin ate.

- **Uranium:**
  - forms halides in oxidation states from +3 to +6.
  - Uranium (VI): UF$_6$ (colorless, does not require use of elemental fluorine to be made, octahedral, volatile), UCl$_6$ (dark green, hydroscopic, octahedral, volatile).
Uranium (V): rare oxidation states, unstable, six and seven coordination.
Uranium (IV): most important uranium halides, U\textsuperscript{+4} does not have reducing tendencies, UI is stable but not to hydrolysis.
Uranium (III): ease of oxidation of U\textsuperscript{+3}, all made under reducing conditions, have typical structure of actinide trihalides, UF\textsubscript{3} (green, 11-coordinate structure), UCl\textsubscript{3} and UBr\textsubscript{3} (red, trigonal prism), UI\textsubscript{3} (8-coordinate, black).

Figure 1: Uraninite, also known as pitchblende, is the most common ore mined to extract uranium. Image used with permission (CC BY-SA 2.5; Joachimsthal).

- Neptunium:
  - has a range of halides in different O.S. but only fluorides are in above +4.
  - has purple and blue-white fluorides, has green chlorides, has green and red-orange and dark red bromides and has brown iodides.
  - NpF\textsubscript{6} forms a toxic and volatile vapor.
  - There also exists oxyhalides, such as NpOF\textsubscript{3} and NpOCl.

- Plutonium:
  - Has a low stability of high O.S.
  - Only consists of trihalides and tetrahalides, but PuF\textsubscript{6} exists though; and it is very volatile, reactive, is best kept in its gas state, does not exist in solid state, and is decomposed by its own radiation.
  - The trihalides have pastel colors: fluoride (violet-blue), chloride (blue-green), bromide (light-green), iodide (bright-green); +2 state is inaccessible.
  - Its complexes are in the +4 state and are stable except for iodides.
  - Its oxyhalides include PuO\textsubscript{2}Cl\textsubscript{2}•H\textsubscript{2}O.

- Americium:
  - The dihalides become insoluble for the first time.
  - They are black solids.
  - Only the fluorides have higher than +3 O.S.
The trihalides are important and have pastel colors: fluoride and chloride are pink, bromide is white-pale yellow, and iodide is pale yellow.

- **Curium(III) Chloride:**
  - Is made by $^{244}\text{Cm}$ isotope which is converted to $^{248}\text{Cm}$ then heated to 1200°C and converted to oxide then chlorinated with HCl at 500°C to create CmCl$_3$.

- **Californium:**
  - The only oxidation state s are +3 and +2 and it only forms chloride and iodide halides.
  - The following are examples of Californium halides: CfCl$_3$, Cf$_3$, and CfI$_2$.

- **Einsteinium:**
  - Its only oxidation state is +3 and it only forms with chloride, fluorine, and even oxygen.
  - The following are examples of Einsteinium halides: Es$_2$O$_3$, EsCl$_3$, EsF$_3$.

### Oxides

All Actinides form oxides with different oxidation states. The most common oxides are of the form M$_2$O$_3$, where M would be one of the elements in the Actinide series. The earliest actinides have a closer relation to the transition metals, where the oxidation state is equal to the number of electrons on the outer shell. The +4 state is more stable in the Actinide series than in the Lanthanides. The following are the different oxides of the Actinide elements:

- M$_2$O$_3$:Ac, Pu-Es
- MO$_2$:Th, U-Cf
- M$_2$O$_5$:Pa, Np
- MO$_3$: U, Np(?)

(?)-Neptunium is unknown in this oxide state, but scientists assume it does exist.

### Oxyhalides

The oxyhalides of Actinides are not binary but some are formed by earlier Actinides, for example, an aqueous Protactinium fluoride reacts with air to make PaO$_2$F, Thorium can form ThOX$_2$, Neptunium can make NpOF$_3$, Plutonium forms PuOF$_4$ and UO$_2$F$_2$ is made by Uranium (III) oxide and Hydrofluoric acid.

### Uranium Hydride ($\text{UH}_3$)

The uranium in uranium hydride has an oxidation state of +3, which is strongly reducing, so it forms a stable hydride. Uranium hydride reacts with hydrogen gas at 250 degrees and swells up into a fine black powder, which is pyrophoric in air. It decomposes at higher temperatures to hydrogen and uranium powders. It can also react with many other compounds at certain temperatures to make halides, oxides, and other compounds, including the following:

- with $\text{HBr}$ to make $\text{UBr}_3$
- with $\text{H}_2\text{O}$ to make $\text{UO}_2$
- with $\text{Cl}_2$ to make $\text{UCl}_4$
- with $\text{HF}$ to make $\text{UF}_4$
• with \( \text{H}_2\text{S} \) to make \( \text{US}_2 \)

Nuclear Fission Reaction of Uranium

\[ ^{235}\text{U} + ^1\text{n} \rightarrow ^{236}\text{U} \rightarrow \text{fission fragments} + \text{neutrons} + 3.20 \times 10^{-11} \text{ J}. \]

235-Uranium is bombarded with neutrons and turns into 236-Uranium. The 236-Uranium then converts into smaller pieces, 2-3 neutrons are released along with energy. These extra neutrons help create a chain reaction as more neutrons come into contact with Uranium. This uncontrolled energy eventually leads to an explosion, which is the basis of the atomic bomb. To see a lab presentation of what this reaction looks like click on the video below.

Alpha Particles

The nucleus of Uranium emits radioactivity in the form of alpha particles. Alpha particles are Helium atoms with the atomic mass of 4 and an atomic number of 2. Alpha particles produce ions but have weak penetrating power that can easily be stopped by sheets of paper. Alpha particles produce large numbers of ions because of their collisions and near collisions with atoms, while traveling through matter. Their positive charge allows them to be deflected by electric and magnetic fields.

By using a nuclear equation and following two rules:

1. The sum of mass numbers must be the same on both sides.
2. The sum of atomic numbers must be the same on both sides we can write equations, such as the following, where \( ^4_2\text{He} \) represents the alpha particle.

\[
\ce{ ^{238}\text{U} \rightarrow ^{234}\text{Th} + ^4_2\text{He}}
\]

The rules for writing a nuclear equation can apply to other radioactive decay processes, such as beta particle or gamma ray decay.

---

**Beta Particles**

Beta particles are deflected by the electric and magnetic fields in the opposite direction from alpha particles. Because they are not as big or massive as alpha particles, they are deflected more strongly than alpha particles are. Beta particles are electrons that came from the nuclei of atoms in nuclear decay processes. Although beta particles do not have actual atomic numbers, its charge is extremely close to the atomic number of -1. Many times a beta particle is small enough that its charge could be ignored during calculations. When we think of beta decay processes, we can look at the following equations and imagine a neutron within the nucleus of an atom converting to a proton or electron spontaneously. The proton remains in the nucleus and the electron is produced as a beta particle. The extra proton causes the atomic number to increase by one unit, but the mass number is unchanged.

- Beta particle-ejected electron from nucleus of U
  \[
  \ce{ ^{239}\text{U} \rightarrow ^{239}\text{Np} + \beta^-}
  \]

- Beta particle-ejected electron from nucleus of Np
  \[
  \ce{ ^{239}\text{Np} \rightarrow ^{239}\text{Pu} + \beta^-}
  \]

- Beta particle-ejected electron from nucleus of U
  \[
  \ce{ ^{237}\text{U} \rightarrow ^{237}\text{Np} + \beta^-}
  \]

- Beta particle-ejected electron from nucleus of Pa
  \[
  \ce{ ^{234}\text{Pa} \rightarrow ^{234}\text{U} + \beta^-}
  \]

- Beta particle-ejected electron from nucleus of Th
  \[
  \ce{ ^{234}\text{Th} \rightarrow ^{234}\text{Pa} + \beta^-}
  \]

---

**Gamma Rays**

Gamma rays (\(\gamma\)) are radiation that is emitted when the nucleus is in an excited state due to excess energy. This energy is then released in the form of gamma rays. Gamma Rays are a form of electromagnetic energy such as
visible light and hence are undeflected by electric and magnetic fields. The following are some examples of gamma ray reactions:

\[
\begin{align*}
\text{^{230}Th + ^1_0n \rightarrow ^{231}Th + \gamma} \\
\text{^{238}U + ^1_0n \rightarrow ^{239}U + \gamma} \\
\text{^{230}Th \rightarrow ^{230}Th + \gamma}
\end{align*}
\]

**Applications**

- Plutonium and Uranium are used as nuclear fuels and in weaponry.
- Thorium (ThO\(_2\)) is used as an incandescent gas mantle from the 1880s. They are now used for cooking, gas lanterns, and for decorative gas lights.
- The 238-Plutonium isotope...
  - Powered the Apollo-12 Lunar Mission’s left behind generator. It generated under 1.5 kW of heat converted to electricity by thermoelectric elements.
  - Was a power source for orbiting satellites and missions to take pictures of Jupiter.
  - Powers pacemakers for the heart. The nuclear energy creates a longer lifetime use of the device.
- The 241-Amercium isotope is used as ionizing sources for smoke detectors.
- Uranium is used in nuclear reactors in the form of fuel in rods suspended in water under a pressure of 70 to 150 atmospheres.

**Problems**

1. Which Actinides were the first to be discovered? Which Actinides were discovered in nature? What makes the Actinides you answered in the first questions different than the rest?
2. For the reaction of Actinium (III) hydroxide with hydrofluoric acid, a) write and balance the equation and b) explain what makes the O.S. of Actinium different than the other Actinides.
3. Explain why isotopes, such as \(^{241}\text{Am}, ^{239}\text{Pu}\) and \(^{237}\text{Np}\) extremely important and the main isotopes for their specific element.
4. What evidence shows that Actinides are very reactive, for the most part?
5. Describe what is happening during a beta particle equation.

**Answers**

1. The first Actinides to be discovered were Thorium and Uranium. The Actinides that were discovered in small portions in nature were Actinium and Protactinium. What makes these different from the rest is they were discovered naturally, and the Actinides all after Uranium were man-made.
2. a) Ac(OH)\(_3\) +3HF+700°Cà AcF\(_3\)+3H\(_2\)O and b) The difference between Actinium and the other Actinides involving O.S. is Actinium only has one O.S. which is +3.
3. Those specific isotopes have various but extremely high half-lives, meaning they decay slowly, which makes it easy for scientists to study and experiment with each of them over long periods of time.
4. The evidence that shows Actinides are very reactive are they have low solubilities as halide compounds; and the lighter, trivalent Actinide compounds are unstable in aqueous solutions and can be easily precipitated out of acidic and basic environments.

5. During a beta particle equation, a neutron within the nucleus of an atom is converted to a proton or electron spontaneously. The proton remains in the nucleus and the electron is produced as a beta particle. The extra proton causes the atomic number to increase by one unit, but the mass number is unchanged.

References