# 7 Lanthanoids and Actinoids

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Lanthanoids and actinoids are *f*-block transition elements, but their general properties differ significantly from those of *d*-block transition metals. These elements are placed in separate positions in the periodic table showing that the periodicity of their electronic structures differs from the main stream. Although lanthanoids are called rare-earth elements, their abundance in the crust is by no means rare and chemistry utilizing their unique properties is likely to develop significantly in the near future. Actinoids are closely related to nuclear chemistry and nuclear energy. Since the amount of superheavy elements "synthesized" in accelerators is very minute, they are not very significant from the viewpoint of applied chemistry.

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## 7.1 Lanthanoids

The fifteen elements shown in Table 7.1 from lanthanum, La ($4f^0$), to lutetium, Lu ($4f^{14}$), are **lanthanoids**. Ln may be used as a general symbol for the lanthanoid elements. Although lanthanoids, scandium, Sc, and yttrium, Y, are sometimes called rare earth elements, they are relatively abundant in the earth's crust. With the exception of promethium, Pm, which does form a stable isotope, even the least abundant thulium, Tm, and lutetium, Lu, are as abundant as iodine. Because lanthanoids have very similar properties and are difficult to separate from one another, they were not useful for basic research and application, and hence they were regarded as rare elements. Since a liquid-liquid solvent extraction method using tributylphosphine oxide became available in the 1960s, lanthanoid elements have been readily available and widely used not only for chemical research but also as materials in alloys, catalysts, lasers, cathode-ray tubes, *etc*.

**Exercise 7.1** What is the difference between lanthanoids and lanthanides?

"Answer" Fifteen elements La-Lu are lanthanoids and fourteen elements Ce-Lu without lanthanum are lanthanides (meaning the elements similar to lanthanum).
Occasionally the names are confused and 15 elements including lanthanum may be called lanthanides.

**Table 7.1** Properties of lanthanoids

| Atomic number | Name | Symbol | Electron configuration | $M^{3+}$ radius (pm) |
|---|---|---|---|---|
| 57 | Lanthanum | La | $5d^16s^2$ | 116 |
| 58 | Cerium | Ce | $4f^15d^16s^2$ | 114 |
| 59 | Praseodymium | Pr | $4f^36s^2$ | 113 |
| 60 | Neodymium | Nd | $4f^46s^2$ | 111 |
| 61 | Promethium | Pm | $4f^56s^2$ | 109 |
| 62 | Samarium | Sm | $4f^66s^2$ | 108 |
| 63 | Europium | Eu | $4f^76s^2$ | 107 |
| 64 | Gadolinium | Gd | $4f^75d^16s^2$ | 105 |
| 65 | Terbium | Tb | $4f^96s^2$ | 104 |
| 66 | Dysprosium | Dy | $4f^{10}6s^2$ | 103 |
| 67 | Holmium | Ho | $4f^{11}6s^2$ | 102 |
| 68 | Erbium | Er | $4f^{12}6s^2$ | 100 |
| 69 | Thurium | Tm | $4f^{13}6s^2$ | 99 |
| 70 | Ytterbium | Yb | $4f^{14}6s^2$ | 99 |
| 71 | Lutetium | Lu | $4f^{14}5d^16s^2$ | 98 |

Because the three stages of ionization enthalpy of lanthanoid elements are comparatively low, they are positive elements and readily assume trivalent ionic states. Most compounds of lanthanoids other than $Ce^{4+}$ ($4f^0$), $Eu^{2+}$ ($4f^7$), $Yb^{2+}$ ($4f^{14}$), are usually $Ln^{3+}$ ones. $Ln^{3+}$ species are hard acids, and since *f* electrons are buried deeply and not used for bonding, they are hardly influenced by ligands. There is a tendency for atomic and ionic radii to decrease with the increase of the atomic number, and this phenomenon is called the **lanthanide contraction**. This contraction is due to small shielding effects of 4 *f* electrons, which causes the atomic nucleus to draw outer shell electrons strongly with an increase of atomic number.

Complexes of lanthanoid metals are 6 to 12 coordinate and especially many 8 and 9 coordinate compounds are known. Organometallic compounds with cyclopentadienyl ligands of the types $Cp_3Ln$ or $Cp_2LnX$ are also known, all of which are very reactive to oxygen or water.

### 7.2 Actinoids

The fifteen elements from actinium, Ac, to lawrencium, Lr, are called **actinoids** (Table 7.2). The general symbol of these elements is An. All the actinoid elements are radioactive and very poisonous. Actinoids that exist in nature in considerable amounts are thorium, Th, protactinium, Pa, and uranium, U, and thorium and uranium are actually isolated from ores and find application. Plutonium metal, Pu, is produced in large quantities in nuclear reactors and its economical efficiency as a fuel for conventional nuclear reactors and fast breeder reactors, as well as its safety, are being examined. As isolable amounts of the elements after americium, Am, are small and their radioactivity is very high, study of their chemical properties is very limited.

**Table 7.2** Properties of actinoids

| Atomic number | Name | Symbol | Electron configuration | $M^{3+}$ radius (pm) | Main isotope |
|---|---|---|---|---|---|
| 89 | Actinium | Ac | $6d^1 7s^2$ | 126 | $^{227}Ac$ |
| 90 | Thorium | Th | $6d^2 7s^2$ | | $^{232}Th$ |
| 91 | Protactinium | Pa | $5f^2 6d^1 7s^2$ | 118 | $^{231}Pa$ |
| 92 | Uranium | U | $5f^3 6d^1 7s^2$ | 117 | $^{235}U$, $^{238}U$ |
| 93 | Neptunium | Np | $5f^5 7s^2$ | 115 | $^{237}Np$ |
| 94 | Plutonium | Pu | $5f^6 7s^2$ | 114 | $^{238}Pu$, $^{239}Pu$ |
| 95 | Americium | Am | $5f^7 7s^2$ | 112 | $^{241}Am$, $^{243}Am$ |
| 96 | Curium | Cm | $5f^7 6d^1 7s^2$ | 111 | $^{242}Cm$, $^{244}Cm$ |
| 97 | Berkelium | Bk | $5f^9 7s^2$ | 110 | $^{249}Bk$ |
| 98 | Californium | Cf | $5f^{10} 7s^2$ | 109 | $^{252}Cf$ |
| 99 | Einsteinium | Es | $5f^{11} 7s^2$ | | |
| 100 | Fermium | Fm | $5f^{12} 7s^2$ | | |
| 101 | Mendelevium | Md | $5f^{13} 7s^2$ | | |
| 102 | Nobelium | No | $5f^{14} 7s^2$ | | |
| 103 | Lawrencium | Lr | $5f^{14} 6d^1 7s^2$ | | |

The process of radioactive disintegration of radioactive elements into stable isotopes is of fundamental importance in nuclear chemistry. If the amount of a radionuclide which exists at a certain time is $N$, the amount of disintegration in unit time is proportional to $N$. Therefore, radioactivity is

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = \lambda N$$

($\lambda$ is disintegration constant)
integration of the equation leads to

$$N = N_0 \mathrm{e}^{-\lambda t}$$

where $N_0$ is the number of atoms at zero time and the time during which the radioactivity becomes half of $N_0$ is the **half life**.

$$T = \frac{\ln 2}{\lambda} = \frac{0.69315}{\lambda}$$

**Exercise 7.2** How does a nuclide change with $\alpha$ disintegration and $\beta^-$ disintegration?

"Answer" Because an atomic nucleus of helium atom, $^4$He, is emitted by $\alpha$ disintegration of a nuclide, its atomic number $Z$ becomes ($Z$-2) and its mass number $A$ changes to ($A$-4). In $\beta^-$ disintegration, an electron is emitted and $Z$ becomes a nuclide ($Z$+1).

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**Isolation of thulium**

Thulium is a rare earth element with the least abundance except promethium, and there were remarkable difficulties in isolating it as a pure metal. P. T. Cleve discovered the element in 1879, but it was only 1911 when the isolation of the metal of almost satisfying purity was reported.

C. James of the United States tried many minerals and found that three ores, ytterspar, euzenite and columbite produced from an island in the northern Norway, were the best source. In order to obtain a purer metal of thulium, chromates of the mixed rare-earth metals obtained by the treatment of a large amount of the ores by sodium hydroxide, hydrochloric acid, oxalic acid, and barium chromate were recrystallized repeatedly from water and water-alcohol. In those days, identification of an element by spectroscopy was already possible, and recrystallizations were repeated 15,000 times over several months, proving that it was not possible to obtain purer metal.

Chemists are requested to repeat monotonous operations even now but it is not likely that patience of this sort still exists. This may hinder the progress of our understanding of the chemistry of rare earth elements.

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Although actinoids are similar to lanthanoids in that their electrons fill the 5*f* orbitals in order, their chemical properties are not uniform and each element has characteristic properties. Promotion of 5*f* - 6*d* electrons does not require a large amount of energy and examples of compounds with $\pi$-acid ligands are known in which all the 5*f*, 6*d*, 7*s*, and 7*p* orbitals participate in bonding. Trivalent compounds are the most common, but other oxidation states are not uncommon. Especially thorium, protactinium, uranium, and neptunium tend to assume the +4 or higher oxidation state. Because their radioactivity level is low, thorium and uranium, which are found as minerals, can be handled legally in a normal laboratory. Compounds such as $ThO_2$, $ThCl_4$, $UO_2$, $UCl_3$, $UCl_4$, $UCl_6$, $UF_6$, *etc*. find frequent use. Especially uranium hexafluoride, $UF_6$, is sublimable and suitable for gas diffusion and undergoes a gas centrifuge process for the separation of $^{235}U$. Thorium is an oxophilic element similar to the lanthanoids.

**Problem**

**7.1** What is the reason for the relatively easy separation of cerium and europium among the lanthanoids, which were difficult to isolate?

**7.2** Calculate the radioactivity after a period of 10 times as long as the half-life of a given material.