7.2: Actinoids

The fifteen elements from actinium, Ac, to lawrencium, Lr, are called **actinoids** (Table 7.2.2). 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 7.2.2 Properties of actinoids

Atomic number	Name	Symbol	Electron configuration	M^{3+} radius (pm)	Main isotope
89	Actinium	Ac	$6d^17s^2$	126	^{227}Ac
90	Thorium	Th	$6d^27s^2$		^{227}Ac
91	Protactinium	Pa	$5f^26d^17s^2$	118	^{232}Th
92	Uranium	U	$5f^36d^17s^2$	117	^{235}U, ^{238}U
93	Neptunium	Np	$5f^57s^2$	115	^{237}Np
94	Plutonium	Pu	$5f^67s^2$	114	^{238}Pu, ^{239}Pu
95	Americium	Am	$577s^2$	112	^{241}Am,^{243}Am
96	Curium	Cm	$5f^76d^17s^2$	111	^{242}Cm, ^{244}Cm
97	Berkelium	Bk	$5f^97s^2$	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	$5f^{14}6d^17s^2$		

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

$$-\frac{dN}{dt} = \lambda N \qquad (\lambda \text{ is disintegration constant})$$

integration of the equation leads to

$$N = n_0 e^{-\lambda t}$$

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 7.2.2

How does a nuclide change with α disintegration and β^- disintegration?

Answer

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

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.

Although actinoids are similar to lanthanoids in that their electrons fill the 5f orbitals in order, their chemical properties are not uniform and each element has characteristic properties. Promotion of 5f - 6d electrons does not require a large amount of energy and examples of compounds with π-acid ligands are known in which all the 5f, 6d, 7s, and 7p 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.

problems

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.