

## RARE EARTH ELEMENTS

**Rare earth elements** - A group of 17 elements, including scandium, yttrium, lanthanum and

lanthanides: cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium.

Rare earth elements show a great similarity between chemical and some physical properties, which is explained by the almost identical structure of the outer electronic levels of their atoms. They are all silver-white metals, and all have similar chemical properties. Rare earth elements are metals, they are obtained by reduction of the corresponding oxides, fluorides, electrolysis of anhydrous salts and other methods.

According to their chemical properties and joint presence in nature, they are divided into subgroups:

- yttrium (Y, La, Gd - Lu);
- ceric (Ce - Eu).

By atomic mass, lanthanides are divided into:

- light (Ce - Eu);
- heavy (Gd - Lu).

The name "rare earths" (from the Latin *terrae rarae* - "rare earths") was given due to the fact that they:

- relatively rare in the earth's crust (content (1.6-1.7) ·10<sup>-2</sup>% by weight);
- form refractory oxides that are practically insoluble in water (such oxides were called "earths" in the early 19th century and earlier).

The name "rare earth elements" was historically formed in the late 18th - early 19th centuries, when it was mistakenly believed that minerals

containing elements of two subfamilies - cerium (light - La, Ce, Pr, Nd, Sm, Eu) and yttrium (heavy - Y , Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) - rarely found in the earth's crust. However, in terms of raw material reserves, rare earth elements are not rare; in terms of their total abundance, they exceed lead by 10 times, molybdenum by 50 times, and tungsten by 165 times.

In 1794, the Finnish chemist Johan Gadolin, examining ore samples near the Swedish town of Ytterby (in the future, the rare earth elements yttrium (Y), terbium (Tb), erbium (Er) and ytterbium (Yb) were named after this village), discovered a previously unknown "Rare earth", which he named after the place of the discovery of yttrium.

Later, the German chemist Martin Klaproth divided these samples into two "lands", for one of which he left the name of yttrium, and the other called cerium (in honor of the small planet Ceres discovered in 1801, which, in turn, was named after the ancient Roman goddess Ceres).

A little later, the Swedish Scientist K. Mosander was able to isolate several more "lands" from the same sample. All of them turned out to be oxides of new elements, called rare earth elements. Due to the complexity of the separation of oxides, false announcements of the discovery of new rare earth elements were counted in the tens. Together, by 1907, chemists had discovered and identified only 16 such elements. Based on the study of X-ray properties, all elements were assigned atomic numbers 21 (scandium), 39 (yttrium), and from 57 (lanthanum) to 71 (lutetium), except 61.

As their atomic weight increases, they are arranged as follows:

Z	Symbol	Name	Etymology
21	Sc	Scandium	in honor of Scandinavia
39	Y	Yttrium	in honor of the Swedish village of Ytterby
57	La	Lanthanum	from the Greek. "secretive"
58	Ce	Cerium	in honor of the minor planet Ceres, in turn named after the goddess Ceres

59	Pr	Praseodymium	from the Greek. "Green twin", due to the green line in the spectrum
60	Nd	Neodymium	from the Greek. "New twin"
61	Pm	Promethium	on behalf of the mythical hero Prometheus, who stole fire from Zeus and handed it over to people.
62	Sm	Samarium	by the name of the mineral samarskite, in which it was discovered
63	Eu	Europium	in honor of Europe
64	Gd	Gadolinium	in honor of Johan Gadolin
65	Tb	Terbium	in honor of the Swedish village of Ytterby
66	Dy	Dysprosium	from the Greek. "Hard to reach"
67	Ho	Holmium	in honor of Stockholm
68	Er	Erbium	in honor of the Swedish village of Ytterby
69	Tm	Thulium	from the old name of Scandinavia
70	Yb	Ytterbium	in honor of the Swedish village of Ytterby
71	Lu	Lutetium	from the ancient Roman name of Paris

## Chemical properties

Scandium, yttrium and lanthanides are highly reactive. The chemical activity of these elements is especially noticeable at elevated temperatures. When heated to 300–400 ° C, metals react even with hydrogen to form  $RH_3$  and  $RH_2$  (the R symbol represents a rare earth atom). These compounds are strong enough and have a saline character. When heated in oxygen, metals easily react with it, forming oxides:  $R_2O_3$ ,  $CeO_2$ ,  $Pr_6O_{11}$ ,  $Tb_4O_7$  (only Sc and Y, through the formation of a protective oxide film, are stable in air, even when heated to 1000 ° C). During the combustion of these metals in an oxygen atmosphere, a large amount of heat is released. The combustion of 1 g of lanthanum releases 224.2 kcal of heat. For cerium, a characteristic feature is the property of pyrophoricity - the ability to sparkle when cutting metal in air.

Lanthanum, cerium and other metals react with water and non-oxidizing acids even at ordinary temperatures, releasing hydrogen. Due to the high activity towards atmospheric oxygen and water, pieces of lanthanum, cerium, praseodymium, neodymium and europium should be stored in

paraffin, the rest of the rare earth metals are poorly oxidized (with the exception of samarium, which is covered with a film of oxides, but not completely corroded by it) and they can store under normal conditions without antioxidants.

The chemical activity of rare earth metals is not the same. From scandium to lanthanum, the chemical activity increases, and in the series of lanthanum - lutetium - it decreases. Hence it follows that lanthanum is the most active metal. This is due to a decrease in the radii of atoms of the elements from lanthanum to lutetium on the one hand, and from lanthanum to scandium on the other.

The effect of "lanthanoid contraction" (compression) leads to the fact that the elements following after lanthanides (hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum) have reduced atomic radii by 0.2-0.3 Å, hence their very similar properties with properties of the corresponding elements of the fifth period.

In the elements - scandium, yttrium, lanthanum - the d-shell of the penultimate electron layer is just beginning to form, so the radii of atoms and the activity of metals in this group increase from top to bottom. This property differs the group from other side subgroups of metals, in which the order of change in activity is opposite.

Rare earth elements most often exhibit an oxidation state of +3. Because of this, the most characteristic oxides are  $R_2O_3$  - solid, strong and refractory compounds. Being basic oxides, for most elements they are able to combine with water and create bases -  $R(OH)_3$ . Rare earth metal hydroxides are poorly soluble in water. The ability of  $R_2O_3$  to combine with water, that is, the main function, and the solubility of  $R(OH)_3$  decrease in the same sequence as the activity of metals:  $Lu(OH)_3$ , and especially  $Sc(OH)_3$ , exhibit some amphoteric properties. So, in addition to the solution of  $Sc(OH)_3$  in concentrated NaOH, the salt obtained:  $Na_3Sc(OH)_6 \cdot 2H_2O$ .

Since the metals of this subgroup are active, and their salts with strong acids are soluble, they easily dissolve in both non-oxidizing acids and oxidizing acids.

All rare earth metals react vigorously with halogens to form  $RHal_3$  (Hal is halogen). They also react with sulfur and selenium, but when heated.

### **Being in nature**

As a rule, rare earth elements occur together in nature. They form very strong oxides, halogen compounds, sulfides. Compounds of trivalent elements are most characteristic of lanthanides. The exception is cerium, which easily passes into a tetravalent state. In addition to cerium, tetravalent compounds form praseodymium and terbium. Divalent compounds are known for samarium, europium and ytterbium. In terms of physicochemical properties, lanthanides are very close to each other. This is due to the peculiarity of the structure of their electronic shells.

The total content of rare earth elements is more than 100 g / t. More than 250 minerals are known to contain rare earth elements. However, only 60 - 65 minerals in which the content of  $Me_2O_3$  exceeds 5 - 8% can be attributed to the actual rare earth minerals. The main rare earth minerals are monazite (Ce, La)  $PO_4$ , xenotime  $YPO_4$ , bastnesite  $Ce [CO_3] (OH, F)$ , parisite  $Ca (Ce, La)_2 [CO_3]_3 F_2$ , gadolinite  $Y_2 Fe Be_2 Si_2 O_{10}$ , ortite  $(Ca, Ce)_2 (Al, Fe)_3 Si_3 O_{12} (O, OH)$ , loparite  $(Na, Ca, Ce) (Ti, Nb) O_3$ , eshinite  $(Ce, Ca, Th) (Ti, Nb)_2 O_6$ . Cerium is the most widespread in the earth's crust, the least is thulium and lutetium. According to the rules of the Commission on New Minerals and Names of Minerals (CNMNM) of the International Mineralogical Association (IMA), minerals with a large amount of a rare earth element (or close to rare earths yttrium and scandium) in the composition receive a special suffix, "Levinson's clarifier", for example, two minerals are known: gagarinite- (Y) with a predominance of yttrium and hagarinite- (Ce) with a predominance of cerium.