Lanthanides: Properties and Reactions

The Lanthanides consist of the elements in the f-block of period six in the periodic table. While these metals can be considered transition metals, they have properties that set them apart from the rest of the elements.

Introduction

The Lanthanides were first discovered in 1787 when a unusual black mineral was found in Ytterby, Sweden. This mineral, now known as Gadolinite, was later separated into the various Lanthanide elements. In 1794, Professor Gadolin obtained yttria, an impure form of yttrium oxide, from the mineral. In 1803, Berzelius and Klaproth secluded the first Cerium compound. Later, Moseley used an x-ray spectra of the elements to prove that there were fourteen elements between Lanthanum and Hafnium. The rest of the elements were later separated from the same mineral. These elements were first classified as 'rare earth' due to the fact that obtained by reasonably rare minerals. However, this is can be misleading since the Lanthanide elements have a practically unlimited abundance. The term Lanthanides was adopted, originating from the first element of the series, Lanthanum.

Like any other series in the periodic table, such as the Alkali metals or the Halogens, the Lanthanides share many similar characteristics. These characteristics include the following:

- Similarity in physical properties throughout the series
- Adoption mainly of the +3 oxidation state. Usually found in crystalline compounds)
- They can also have an oxidation state of +2 or +4, though some lanthanides are most stable in the +3 oxidation state.
- Adoption of coordination numbers greater than 6 (usually 8-9) in compounds
- Tendency to decreasing coordination number across the series
- A preference for more electronegative elements (such as O or F) binding
- Very small crystal-field effects
- Little dependence on ligands
- Ionic complexes undergo rapid ligand-exchange

Electron Configuration

Similarly, the Lanthanides have similarities in their electron configuration, which explains most of the physical similarities. These elements are different from the main group elements in the fact that they have electrons in the f orbital. After Lanthanum, the energy of the 4f sub-shell falls below that of the 5d sub-shell. This means that the electron start to fill the 4f sub-shell before the 5d sub-shell.

The electron configurations of these elements were primarily established through experiments. The technique used is based on the fact that each line in an emission spectrum reveals the energy change involved in the transition of an electron from one energy level to another. However, the problem with this technique with respect to the Lanthanide elements is the fact that the 4f and 5d sub-shells have very similar energy levels, which can make it hard to tell the difference between the two.

Another important feature of the Lanthanides is the Lanthanide Contraction, in which the 5s and 5p orbitals penetrate the 4f sub-shell. This means that the 4f orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease that continues throughout the series.

Table 1: Electron Configurations of the Lanthanide Elements

Symbol	Idealized	Observed	Symbol	Idealized	Observed
La	$5d^16s^2$	$5d^16s^2$	Tb	$4f^85d^16s^2$	$4f^9\ 6s^2$ or $4f^85d^16s^2$
Ce	$4f^15d^16s^2$	$4f^15d^16s^2$	Dy	$4f^95d^16s^2$	$4f^{10}\ 6s^2$
Pr	$4f^25d^16s^2$	$4f^3\ 6s^2$	Ho	$4f^{10}5d^16s^2$	$4f^{11}\ 6s^2$
Nd	$4f^35d^16s^2$	$4f^4\ 6s^2$	Er	$4f^{11}5d^16s^2$	$4f^{12}\ 6s^2$
Pm	$4f^45d^16s^2$	$4f^5\ 6s^2$	Tm	$4f^{12}5d^16s^2$	$4f^{13}\ 6s^2$
Sm	$4f^55d^16s^2$	$4f^6\ 6s^2$	Yb	$4f^{13}5d^16s^2$	$4f^{14}\ 6s^2$
Eu	$4f^65d^16s^2$	$4f^7\ 6s^2$	Lu	$4f^{14}5d^16s^2$	$4f^{14}5d^16s^2$

Symbol	Idealized	Observed	Symbol	Idealized	Observed
Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1 6s^2$			

Properties and Chemical Reactions

One property of the Lanthanides that affect how they will react with other elements is called the basicity. Basicity is a measure of the ease at which an atom will lose electrons. In another words, it would be the lack of attraction that a cation has for electrons or anions. In simple terms, basicity refers to have much of a base a species is. For the Lanthanides, the basicity series is the following:

$$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$$

In other words, the basicity decreases as the atomic number increases. Basicity differences are shown in the solubility of the salts and the formation of the complex species. Another property of the Lanthanides is their magnetic characteristics. The major magnetic properties of any chemical species are a result of the fact that each moving electron is a micromagnet. The species are either diamagnetic, meaning they have no unpaired electrons, or paramagnetic, meaning that they do have some unpaired electrons. The diamagnetic ions are: La^{3+}, Lu^{3+}, Yb^{2+} and Ce^{4+}. The rest of the elements are paramagnetic.

Metals and their Alloys

The metals have a silvery shine when freshly cut. However, they can tarnish quickly in air, especially Ce, La and Eu. These elements react with water slowly in cold, though that reaction can happen quickly when heated. This is due to their electropositive nature. The Lanthanides have the following reactions:

- oxidize rapidly in moist air
- dissolve quickly in acids
- reaction with oxygen is slow at room temperature, but they can ignite around 150-200 °C
- react with halogens upon heating
- upon heating, react with S, H, C and N

Table 2: Properties of the Lathanides

Symbol	Ionization Energy (kJ/mol)	Melting Point (°C)	Boiling Point (°C)
La	538	920	3469
Ce	527	795	3468
Pr	523	935	3127
Nd	529	1024	3027
Pm	536		
Sm	543	1072	1900
Eu	546	826	1429
Gd	593	1312	3000
Tb	564	1356	2800
Dy	572	1407	2600
Ho	581	1461	2600
Er	589	1497	2900
Tm	597	1545	1727
Yb	603	824	1427
Lu	523	1652	3327

Periodic Trends: Size

The size of the atomic and ionic radii is determined by both the nuclear charge and by the number of electrons that are in the electronic shells. Within those shells, the degree of occupancy will also affect the size. In the Lanthanides, there is a decrease in atomic size from La to Lu. This decrease is known as the Lanthanide Contraction. The trend for the entire periodic table states that the atomic radius decreases as you travel from left to right. Therefore, the Lanthanides share this trend with the rest of the elements.

Table 3: Periodic Trends

Element	Atomic Radius (pm)	Ionic Radius (3+)	Element	Atomic Radius (pm)	Ionic Radius (3+)
La	187.7	106.1	Tb	178.2	92.3
Ce	182	103.4	Dy	177.3	90.8
Pr	182.8	101.3	Ho	176.6	89.4
Nd	182.1	99.5	Er	175.7	88.1
Pm	181	97.9	Tm	174.6	89.4
Sm	180.2	96.4	Yb	194.0	85.8
Eu	204.2	95.0	Lu	173.4	84.8
Gd	180.2	93.8			

Color and Light Absorbance

The color that a substance appears is the color that is reflected by the substance. This means that if a substance appears green, the green light is being reflected. The wavelength of the light determines if the light with be reflected or absorbed. Similarly, the splitting of the orbitals can affect the wavelength that can be absorbed. This is turn would be affected by the amount of unpaired electrons.

Table 4: Unpaired Electrons and Color

Ion	Unpaired Electrons	Color	Ion	Unpaired Electrons	Color
La^{3+}	0	Colorless	Tb^{3+}	6	Pale Pink
Ce^{3+}	1	Colorless	Dy^{3+}	5	Yellow
Pr^{3+}	2	Green	Ho^{3+}	4	Pink; yellow
Nd^{3+}	3	Reddish	Er^{3+}	3	Reddish
Pm^{3+}	4	Pink; yellow	Tm^{3+}	2	Green
Sm^{3+}	5	Yellow	Yb^{3+}	1	Colorless
Eu^{3+}	6	Pale Pink	Lu^{3+}	0	Colorless
Gd^{3+}	7	Colorless			

Occurrence in Nature

Each known Lanthanide mineral contains all the members of the series. However, each mineral contains different concentrations of the individual Lanthanides. The three main mineral sources are the following:

- Monazite: contains mostly the lighter Lanthanides. The commercial mining of monazite sands in the United States is centered in Florida and the Carolinas
- Xenotime: contains mostly the heavier Lanthanides
- Euxenite: contains a fairly even distribution of the Lanthanides

In all the ores, the atoms with a even atomic number are more abundant. This allows for more nuclear stability, as explained in the Oddo-Harkins rule. The Oddo-Harkins rule simply states that the abundance of elements with an even atomic number is greater than the abundance of elements with an odd atomic number. In order to obtain these elements, the minerals must go through a separating process, known as separation chemistry. This can be done with selective reduction or oxidation. Another possibility is an ion-exchange method.

The Oddo-Harkins Rule

The abundance of elements with an even atomic number is **greater** than the abundance of elements with an odd atomic number.

Applications

Metals and Alloys

The pure metals of the Lanthanides have little use. However, the alloys of the metals can be very useful. For example, the alloys of Cerium have been used for metallurgical applications due to their strong reducing abilities.

Non-nuclear

The Lanthanides can also be used for ceramic purposes. The almost glass-like covering of a ceramic dish can be created with the lanthanides. They are also used to improve the intensity and color balance of arc lights.

Nuclear

Like the Actinides, the Lanthanides can be used for nuclear purposes. The hydrides can be used as hydrogen-moderator carriers. The oxides can be used as diluents in nuclear fields. The metals are good for being used as structural components. The can also be used for structural-alloy-modifying components of reactors. It is also possible for some elements, such as Tm, to be used as portable x-ray sources. Other elements, such as Eu, can be used as radiation sources.

Practice Problems

1. Which elements are considered to be Lanthanides?
2. How do the Lanthanides react with oxygen?
3. What causes the Lanthanide Contraction?
4. Why do Lanthanides exhibit strong electromagnetic and light properties?
5. What do the Lanthanides have in common with the Noble Gases?

Answers

1. Elements Lanthanum (57) through Lutetium (71) on the periodic table are considered to be Lanthanides.
2. Lanthanides tend to react with oxygen to form oxides. The reaction at room temperature can be slow while heat can cause the reaction to happen rapidly.
3. The Lanthanide Contraction refers to the decrease in atomic size of the elements in which electrons fill the f-subshell. Since the f sub-shell is not shielded, the atomic size will decrease as the nuclear charge still increases.
4. Lanthanides exhibit strong electromagnetic and light properties because of the presence of unpaired electrons in the f-orbitals. The majority of the Lanthanides are paramagnetic, which means that they have strong magnetic fields.
5. Both the Lanthanides and Noble Gases tend to bind with more electronegative atoms, such as Oxygen or Fluorine.

References

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