INORGANIC CHEMISTRY

Topic: 5

LANTHANIDES

LONG ANSWER QUESTIONS

1. What are the general characteristics of Lanthanides..

Ans: F – BLOCK ELEMENTS

The elements in which the differentiating electron enters the anti penultimate energy level i.e. (n – 2)f, are called f – block elements. These are often called as inner transition elements or rare earth elements. The differentiating electron in transition elements may enter either 4f or 5f orbitals based upon which they are differentiated into lanthanides and actinides.

Lanthanides

In lanthanides the differentiating electron enters 4f orbital. These are cerium to lutetium. The name lanthanide is because they come immediately after lanthanum.

Actinides In actinides the differentiating electron enters 5f orbitals. These are thorium to lawrencium. These elements come immediately after actinium.

Electronic configuration:

General electronic configuration of f – block elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

Lanthanides $[Xe]4f^{1-14}5d^{0-1}6s^2$

Actinides $[Rn]5f^{1-14}6d^{0-1}7s^2$

CHARACTERISTICS OF LANTHANIDES

1. Oxidation states

Lanthanides show only one stable oxidation state, which is not in the case of actinides. The typical oxidation state of lanthanides is +3. Some elements show +2 and +4 also, when they lead to

(a) a noble gas configuration e.g. $Ce^{4+}(f^0)$

(b) a half filled f shell e.g. $Eu^{2+}(f^7)$

(c) a completely filled f shell e.g. $YB^{22+}(f^{14})$

2. Lanthanide contraction
In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding of f orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.

Consequences of lanthanide contraction
Since the change in ionic radii in lanthanides is very small (only 15 pm from Ce^{3+} to Cu^{3+}), their chemical properties are similar. This makes the separation of the elements in pure state very difficult.

Due to lanthanide contraction, the difference in size between second (4d) and third (5d) is very small.

As the size of the lanthanide ions decreases from La^{+3} to Lu^{+3}, the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic.

3. Complex formation

The lanthanides do not have much tendency to form complexes due to low charge density because of their size. However, the tendency to form complex and their stability increases with increasing atomic number.

4. Chemical Behaviour
The first few members of the series are quite reactive like calcium. However with increasing atomic number, their behaviour becomes similar to that of aluminum.

(a) They combine with H_2 on gentle heating. When heated with carbon, they form carbides. On burning in the presence of halogens, they form halides.

(b) They react with dilute acids to liberate H_2.

(c) They form oxides and hydroxides of the type N_2O_3 and $M(OH)_3$ which are basic alkaline earth metal oxides and hydroxides.

2. **What are the oxidation states exhibited by the Lanthanide elements? Write a note with at least one example each.**

Ans: **Oxidation states**
Lanthanides exhibit different oxidation states like +2, +3 and +4. Among these +3 is the most stable oxidation state. The elements that attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation states.

Example: Europium and ytterbium exhibits +2 and +3 oxidation states - cerium exhibits +4 oxidation state.

Most stable oxidation state of lanthanides is +3. Oxidation states + 2 and + 4 also exist but they revert to +3 e.g. Sm^2+, Eu^{2+}, Yb^{2+} lose electron to become +3 and hence are good reducing agents, where as Ce^{4+}, Pr^{4+}, Tb^{4+} in aqueous solution gain electron to become + 3 and hence are good oxidizing agents. There is a large gap in energy of 4 f and 5 d sub shells and thus the number of oxidation states is limited.

3. **What is meant by Lanthanide contraction? Explain in brief.**

Ans: Lanthanide contraction: The regular decrease in the size of lanthanide ions from atomic number 58, Cerium to 71, Lutetium to is known as lanthanide contraction. It is due to greater effect of the increased nuclear charge than that of the screening effect. In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding of f orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.

Consequences of lanthanide contraction

(a) It results in slight variation in their chemical properties which helps in their separation by ion exchange

(b) Each element beyond lanthanum has same atomic radius as that of the element lying above it in the group
(e.g. Zr 145 pm, Hf 144 pm); Nb 134 pm, Ta 134 pm ; Mo 129 pm, W 130 pm).

(c) The covalent character of hydroxides of lanthanides increases as the size decreases from La^{3+} to Lu^{3+} . However basic strength decreases. La $(OH)_3$Thus is most basic whereas Lu $(OH)_3$ is least basic. Similarly, the basicity of oxides also decreases in the order from La^{3+} to Lu^{3+}.

(d) Tendency to form stable complexes from La^{3+} to Lu^{3+} increases as the size decreases in that order.

(e) There is a slight increase in electronegativity of the trivalent ions from La to Lu.

(f) Since the radius of Yb^{3+} ion (86 pm) is comparable to the heavier lanthanides Tb, Dy, Ho and Er, therefore they occur together in natural minerals.

SHORT ANSWER QUESTIONS

1. **Write any two methods of obtaining Lanthanide metals.**

Ans: Lanthanides are separated from monazite and are converted in to chlorides or oxides.

Then the metals are obtained either by the electrolysis of molten chlorides or by the reduction of the anhydrous halides with strong electropositive metals as Na, Mg etc.

2. **Mention the chemical properties of Lanthanides.**

Ans: Lanthanum exhibits two oxidation states, +3 and +2, the former being much more stable. For example, LaH_3 is more stable than LaH_2.Lanthanum burns readily at 150 °C to form lanthanum (III) oxide:

$$4\,La + 3\,O_2 \rightarrow 2\,La_2O_3$$

However, when exposed to moist air at room temperature, lanthanum oxide forms a hydrated oxide with a large volume increase.

Lanthanum is quite electropositive and reacts slowly with cold water and quite quickly with hot water to form lanthanum hydroxide:

$$2\,La\,(s) + 6\,H_2O\,(l) \rightarrow 2\,La(OH)_3\,(aq) + 3\,H_2\,(g)$$

Lanthanum metal reacts with all the halogens. The reaction is vigorous if conducted at above 200 °C:

$$2\,La\,(s) + 3\,F_2\,(g) \rightarrow 2\,LaF_3\,(s)$$
$$2\,La\,(s) + 3\,Cl_2\,(g) \rightarrow 2\,LaCl_3\,(s)$$
$$2\,La\,(s) + 3\,Br_2\,(g) \rightarrow 2\,LaBr_3\,(s)$$
$$2\,La\,(s) + 3\,I_2\,(g) \rightarrow 2\,LaI_3\,(s)$$

Lanthanum dissolves readily in dilute sulfuric acid to form solutions containing the La(III) ions, which exist as $[La(OH_2)_9]^{3+}$ complexes:

3. **Explain Lanthanide contraction.**

Ans: Lanthanide contraction
In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding of f orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.

Consequences of lanthanide contraction

Since the change in ionic radii in lanthanides is very small (only 15 pm from Ce^{3+} to Cu^{3+}), their chemical properties are similar. This makes the separation of the elements in pure state very difficult.

Due to lanthanide contraction, the difference in size between second (4d) and third (5d) is very small.

As the size of the lanthanide ions decreases from La^{+3} to Lu^{+3}, the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic.

4. **Why Lanthanides exhibit variable valency?**

Ans: Lanthanides exhibit different oxidation states like +2, +3 and +4. Among these +3 is the most stable oxidation state. The elements that attain stable electronic configuration by losing 2 or 4 electrons exhibit +2 and +4 oxidation states.

Example: Europium and ytterbium exhibits +2 and +3 oxidation states - cerium exhibits +4 oxidation state.

Most stable oxidation state of lanthanides is +3. Oxidation states + 2 and + 4 also exist but they revert to +3 e.g. Sm^2+, Eu^{2+}, Yb^{2+} lose electron to become +3 and hence are good reducing agents, where as Ce^{4+}, Pr^{4+}, Tb^{4+} in aqueous solution gain electron to become + 3 and hence are good oxidizing agents. There is a large gap in energy of 4 f and 5 d subshells and thus the number of oxidation states is limited.

F – BLOCK ELEMENTS

The elements in which the differentiating electron enters the anti penultimate energy level i.e. (n – 2)f, are called f – block elements. These are often called as inner transition elements or rare earth elements. The differentiating electron in transition elements may enter either 4f or 5f orbitals based upon which they are differentiated into lanthanides and actinides.

Lanthanides

In lanthanides the differentiating electron enters 4f orbital. These are cerium to lutetium. The name lanthanides is because they come immediately after lanthanum.

Actinides In actinides the differentiating electron enters 5f orbitals. These are thorium to lawrencium. These elements come immediately after actinium.

Electronic configuration:

General electronic configuration of f – block elements is $(n\text{–}2)f^{1\text{–}14}(n\text{–}1)d^{0\text{–}1}ns^2$

Lanthanides $[Xe]4f^{1\text{–}14}5d^{0\text{–}1}6s^2$

Actinides $[Rn]5f^{1\text{–}14}6d^{0\text{–}1}7s^2$

CHARACTERISTICS OF LANTHANIDES

1. Oxidation states

Lanthanides show only one stable oxidation state, which is not in the case of actinides. The typical oxidation state of lanthanides is +3. Some elements show +2 and +4 also, when they lead to

(a) a noble gas configuration e.g. $Ce^{4+}(f^0)$

(b) a half filled f shell e.g. $Eu^{2+}(f^7)$

(c) a completely filled f shell e.g. $YB^{22+}(f^{14})$

2. Lanthanide contraction

In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding of f orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.

Consequences of lanthanide contraction
Since the change in ionic radii in lanthanides is very small (only 15 pm from Ce^{3+} to Cu^{3+}), their chemical properties are similar. This makes the separation of the elements in pure state very difficult.

Due to lanthanide contraction, the difference in size between second (4d) and third (5d) is very small.

As the size of the lanthanide ions decreases from La^{+3} to Lu^{+3}, the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic.

3. Complex formation

The lanthanides do not have much tendency to form complexes due to low charge density because of their size. However, the tendency to form complex and their stability increases with increasing atomic number.

4. Chemical Behaviour

The first few members of the series are quite reactive like calcium. However with increasing atomic number, their behaviour becomes similar to that of aluminum.

(a) They combine with H_2 on gentle heating. When heated with carbon, they form carbides. On burning in the presence of halogens, they form halides.

(b) They react with dilute acids to liberate H_2.

(c) They form oxides and hydroxides of the type N_2O_3 and $M(OH)_3$ which are basic alkaline earth metal oxides and hydroxides.