

E-Content

B.Sc. 2nd Year

Inorganic Chemistry Paper-I

UNIT-III

Chapter - 4

PART-II

THE CHEMISTRY OF LANTHANIDES



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Chapter 4

Unit-3

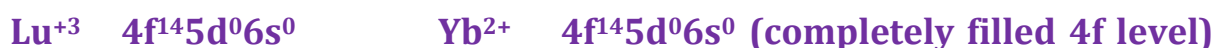
PART-II

Oxidation States Of Lanthanides

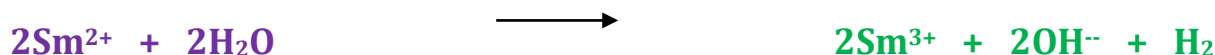
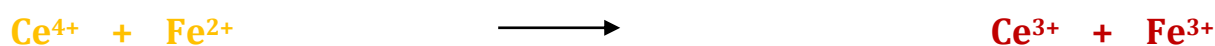
Lanthanides exhibits a principal oxidation state of +3 in which f-subshell contains zero(0) electrons and an underlying layer containing up to 14 electrons(**i.e. f^0 - f^{14}**). The +3 ions of La, Gd and Lu which contain respectively an empty, a half-filled, and a completely filled 4f level are especially stable state. Ce can exhibit an oxidation state of +4 in which it has the same electronic structure with La^{+3} i.e. an empty 4f level and acquire noble gas configuration of xenon. Also, Tb^{4+} which has the same electronic structure as Gd^{3+} i.e. a half-filled 4f level an empty, a half- filled and a completely filled 4f shell confers some extra stability on a particular oxidation state.



Also, Eu^{+2} is isoelectronic with Gd^{+3} i.e. half-filled 4f level and Yb^{+2} is isoelectronic with Lu^{+3}



In addition, to +3 oxidation state +2 and +4 states are also exist for some elements . For example, Sm^{+2} and Tm^{+2} occur with f^6 and f^{13} arrangements and Pr^{4+} and Nd^{4+} have f^1 and f^2 arrangements. The most stable oxidation state is Ln^{3+} and Ln^{2+} and Ln^{4+} are less stable. Ce^{4+} is strongly oxidizing and Sm^{2+} is strongly reducing property:



{Ce⁴⁺ and Sm²⁺ are converted to +3 state, showing that it is the most stable oxidation state}.

Chemical properties of the compounds of various oxidation states

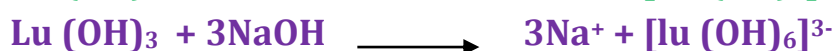
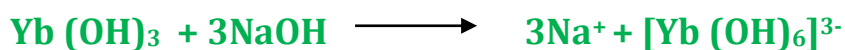
(a) Oxidation State (+3) : The trivalent state is characteristics of all the lanthanides. The standard electrode potential (EP) are all high and vary in a regular way over a small range (-2.48 to -2.26 volts) depending on the size. They are more reactive than aluminum (-1.66 volts) and slightly more than magnesium(-2.36volts).

(i). Hydroxides: Based on their reactivity, they react slowly with cold water, but more rapidly on heating they form to the hydroxide.



The hydroxides which are definite compounds are precipitated as gelatinous precipitates by the addition of NH₄OH to aqueous solutions. They can be obtained in the crystalline form by aging Ln₂O₃ in strong alkali at high temperature and pressure. They are ionic and basic. They are less basic than Ca (OH)₂ but more basic than Al (OH)₃ which is amphoteric. The hydroxides are basic enough as to absorb CO₂ and form carbonates.

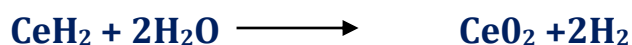
The basicities of the hydroxides decreases with increasing atomic number as will be expected for decreasing ionic radii. Ce (OH)₃ is the most basic while Lu (OH)₃ is the least basic. The decrease in basic properties can be seen by dissolving the of the later members in hot concentrated sodium hydroxide which produces complexes.



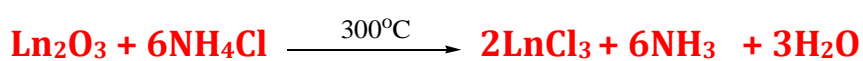
(ii). Oxides: The metals readily tarnish in air and on heating in oxygen, they all give the oxides, Ln₂O₃ which resembles Ca to Ba group Cerium alone forms CeO₂. They oxides are also ionic and basic and readily reacts with water to give the hydroxides. Yb and Lu form a protective oxide film which prevents the whole metal forming oxide unless heated to 1000°C.

(iii). Hydrides: The hydrides are formed when the metal reacts with H₂.

This requires heating up to 300- 4000°C to initiate the reaction. The products-dihydrides, (LnH₂) are solids: black, metallic and conduct electricity. This is because the Ln ion exists in the +3 and has 2H⁻ ion and an electron which occupies a conduction band. Exceptions are Eu and Yb which form the divalent compounds; EuH₂ and YbH₂. These are salt-like and contain M²⁺ and two H⁻. Yb forms non-stoichiometric hydrides approximately YbH_{2.5}. The hydrides generally, liberate hydrogen from water, are stable to heat up to 900°C and react with O₂ to form the oxide. The dihydrides take up H when heated under pressure and all but Eu form salt like hydrides LnH₃ (which has Ln³⁺ and three H⁻) since there are no delocalized electron, they do not show metallic conduction.



(iv). Halides: The anhydrous halides LnX₃ can be prepared by heating the metal and the halogen. It can also be prepared by heating the oxide with an excess of ammonium halide.



The fluorides are of particular importance among the halides, because of their insolubility. Addition of HF acid or Na⁺F⁻ precipitates the fluorides from the Ln³⁺ solutions and this is a characteristic test for lanthanides. The fluorides, particularly of the heavier lanthanides (with smaller Ln ions) are slightly soluble in excess HF owing to formation of soluble complex [LnF(H₂O)_n]²⁺. They may be re dissolved in 3M nitric acid saturated with boric acid, which removes F⁻ as BF₄⁻. The chlorides are deliquescent, soluble in water from which they crystallize as hydrates (with Ce to Nd having 7H₂O and Nd to Lu having 6H₂O). If the hydrated halides are heated, they form oxo halides instead of dehydrating to anhydrous halides. However, cerium gives CeO₃. The bromides and are similar to chlorides.



(iv). Carbides: The lanthanides also form carbides of stoichiometry LnC₂ and Ln₄(C₂)₃. They are formed by the arc melting of the metal with carbon in an inert atmosphere. They can also be formed by reducing the oxides

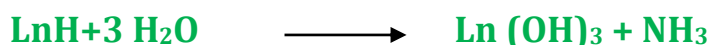
Ln_2O_3 , with carbon in an electric furnace. The lanthanide carbides, LnC_2 are more reactive than CaC_2 . They react with water to give ethyne, hydrogen, ethene and finally ethane. They are best described as acetylides of Ln^{3+} , C_2^{2-} and the extra electron in the conduction band which makes it show metallic conductivity.



(vi). Reaction with other elements: Numerous other compounds are obtained by direct reaction of the lanthanides at elevated temperature with some elements of group (VA) elements ($\text{X}=\text{N}, \text{P}, \text{As}, \text{Sb}$ or Bi). The sulphides are formed by reaction of the chloride with hydrogen sulphide at 1100°C . The lanthanides also react with boron at elevated temperature to give borides, LnB_4 and LnB_6 .



with the group V elements they form LnX etc. that have NaCl structure. LnN is hydrolyzed by water in a similar way like AlN .



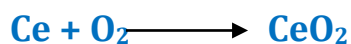
(vii) Oxo salts: Oxo salts of lanthanides also exist which includes nitrates, sulphates, phosphates, carbonates, oxalates etc. Examples are the hydrated salts of common acids which contain the ions $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$, which are readily obtained by dissolving the oxide in acid and crystallizing. Others are double salts which are very common such as,



(b). Oxidation State (+4) -This oxidation state is most important to cerium and a little to praseodymium and terbium. $\text{Ce}(4+)$ is the only $\text{Ln}(4+)$ that exists in solution.

(i). Cerium (IV): The high charge of the ion leads it being heavily hydrated and except in strongly acidic solutions, the hydrated Ce^{4+} will be hydrolyzed giving polymeric species and H^+ . Cerium (IV) in solution (also called ceric) is obtained by treatment of Ce(III) solutions with very powerful oxidizing agents e.g. ammonium peroxodisulphate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or bismuthate in nitric acid.. Solid ceric compounds include CeO_2 , $\text{CeO}_2 \cdot n\text{H}_2\text{O}$

and CeF_4 . CeO_2 is white when pure and is obtained by heating the metal or $\text{Ce}(\text{OH})_3$ or $\text{Ce}_2^{III}(\text{oxalates})_3$ in air or oxygen. It is rather inert, not being attacked by either strong acids or alkalis. However, it can be dissolved by acids in the presence of reducing agents (H_2O_2 , Sn^{2+}) giving Ce^{3+} in solution.



The hydrous oxide, $\text{CeO}_2 \cdot n\text{H}_2\text{O}$, is a yellow gelatinous precipitate. It can be obtained on treating $\text{Ce}(\text{IV})$ solution with bases. It re-dissolves fairly easily in acid. CeF_4 is white compound and has a three-dimensional crystal structure with the metal in at the Centre of a square antiprism. It is easily hydrolyzed by water. It is obtained by treating CeCl_3 or CeF_3 with fluorine at room temperature. Many stable complex ions are formed for example, $[\text{Ce}(\text{NO}_3)_6]^{2-}$ ion or (ammonium cerium (IV) nitrate $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]^{2-}$ where bidentate NO_3^- ions afford 12-coordination.

(iii). Other Lanthanides (IV): The elements of Pr, Nd, Tb and Dy also form compounds of (+IV) states which are generally unstable in water, occur only as solids and form only oxides, fluorides and a few fluoro complexes. Examples are PrO_2 , PrF_4 , $\text{Na}_2[\text{PrF}_6]$, TbO_2 , TbF_4 , DyF_4 , and $\text{Cs}_3[\text{DyF}_7]$.

Oxidation State (+2): Only lanthanide elements Sm, Eu and Yb have aqueous chemistry at oxidation state (+II). $[\text{Sm}^{2+}$, Eu^{2+} and $\text{Yb}^{2+}]$. The most stable is Eu^{2+} which is stable in water but the solution is strongly reducing. The $\text{Eu}^{2+}(\text{aq})$ ion is readily obtained by reducing $\text{Eu}^{3+}(\text{aq})$ with Zn, Zn/Hg, Mg or electrolysis. $\text{Eu}(\text{II})$ bears strong similarities to Calcium in many ways; the insolubility of their sulphates and carbonates in water, the insolubility of the dichloride in strong HCl and the solubility of the metals in liquid NH_3 . They however differ in that the dihalides EuX_2 have a magnetic moment of 7-9BM showing 7 unpaired electrons, whereas Ca compounds are diamagnetic. Sm^{2+} , Yb^{2+} can be obtained by the electrolytic reduction of their trivalent ions in aqueous solution. They are readily oxidized by air and form sulphates, hydroxide, carbonates, halides and phosphates. They form solid dihalide compounds, LnCl_2 and LnI_2 . The dihalides compounds have 8- coordinated Ln_{2+} ions while 7-coordination is

found in EuI_2 . The LnX_2 compounds react with donor solvents to give solvates
e.g. $\text{LnX}_2(\text{THF})_x$

Ores Or Minerals Of Lanthanides

The main ores of Lanthanides are divided into two groups first Cerium group and second Yttrium group.

1. **Cerium Group**- Following ores are comes into this group.

(i) **Monazite sand**- It represent by formula $\text{Ce}(\text{PO}_4)$ and composed of **49-70% Cerium earth** (element of atomic number 57 to 62 as oxide)

1-4% Y earth atomic number 63-71.

5-10% ThO_2

1-2% SiO_2

22-30% P_2O_5 and traces of Uranium.

Found in India, Brazil, South Africa

(ii) **Cerrite** - $(\text{Ce})_3\text{M}^{\text{III}}\text{H}_3\text{Si}_3\text{O}_{11}$

51-72% Cerium earth

7-6% Y earth and traces of Th, Zr, U, etc. found in Sweden.

(iii) **Bastnaesite** CeFCO_3

65-70% Cerium earth

Upto 1% Y earth

2. **Yttrium groups**

Gadolinite or Yttrivite - $(\text{Y})_2\text{M}^{\text{III}}\text{Si}_2\text{O}_{10}$ or $(\text{Be,Fe})_3(\text{Y})_2\text{Si}_2\text{O}_{10}$

35-48% Y earth as oxide

2-17% cerium earth

Upto 11.6% BeO and traces of ThO_2

Extraction and separation of the lanthanides From its Ores

They are extracted from the above mentioned ores Monozite..

Monazite is treated with hot concentrated H_2SO_4 . Th, La and the other Lanthanides dissolved as sulphates and are separated from insoluble material. Th is precipitated ThO_2 by partial neutralization with NH_4OH . Na_2SO_4 used to salt out La and the lighter Ln (Ln=Lanthanide) as sulphates, leaving the heavy lanthanides in solution.

The light Ln are oxidized with bleaching powder Ca(OCl)_2 . Ce^{2+} is oxidized to Ce^{4+} which is precipitated as Ce (IO)_3 and removed. The extraction process from bastnaesite is slightly simpler since it does not contain Th. The different lanthanides elements can be separated by various methods;

1.Reduction of their Trihalides: La, Ce, Pr, Nd and Gd may be obtained by reduction of their trichlorides with calcium at about 1000°C in an argon filled vessel e.g.

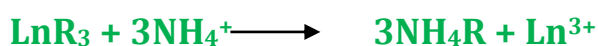
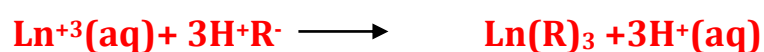


The heavier Ln like Tb, Dy, 110, Er and Tm can also be obtained by this method but the trifluorides are used, since their trichloride is volatile. Also, since the heavier Ln have higher melting points and so require a temperature of 1400°C . At this temperature CaCl_2 boils. Li is sometimes used instead of Ca.



Eu, Sm and Yb are obtained by chemical reduction of their trioxides.

2. A Modern Method or Ion exchange method: The basis of the lanthanide series separation on an ion exchange column is their ability to form complex ions. All lanthanides form $+3$ ions, M^{+3} whose ionic radii decrease progressively with increasing atomic number from Ce^{+3} to Lu^{+3} . As a solution containing $+3$ lanthanides ions is placed at the top of a column of cation exchange resin [e.g. is Dowex-50 made of a sulphurated polystyrene cation exchange resin and contains functional groups $-\text{SO}_3\text{H}$]. The Ln^{+3} ions are absorbed into this resin and an equivalent amount of hydrogen ions are released from the column;



Then elution process is done by eluting solvent like a citrate buffer (citric acid/ammonium citrate) solution (which complexes with the lanthanide ions) is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution. Since the smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column. By the correct choice of conditions, the lutetium ion, $\text{Lu}^{+3}(\text{aq})$, emerges first from the column, followed by the cation's ytterbium, thulium, erbium, etc., in order

of increasing ionic radius. By using a long ion-exchange column, the elements may be obtained at 99-9% with one attempt.

3. Change to Valency or oxidation state method: The different properties of the various oxidation states make separation very easy [i.e. the properties of Ln^{+4} and Ln^{+2} is much different from that of Ln^{+3}]. Cerium can be separated from Ln mixtures because it is the only one which has a Ln^{+4} ions stable in aqueous solution. A solution containing mixture of Ln^{+3} ions can be oxidized with NaOCl under alkaline conditions to produce Ce^{+4} . Because of the higher charge, Ce^{+4} is much smaller and less basic than Ce^{+3} or any other Ln^{+3} . The Ce^{+4} is separated by carefully controlled precipitation of CeO_2 or leaving the trivalent ions in solution. Also, Eu^{2+} can be separated from a mixture of Ln^{+3} . If a solution of Ln^{+3} ions is reduced electrolytically using a Hg cathode or Zn amalgam, then Eu^{2+} is produced. If H_2SO_4 is present, EuSO_4 which is insoluble will be This can be filtered off.

Other methods used for separation are Solvent Extraction, Precipitation, Fractional crystallization, Complex formation and Thin layer chromatography (TLC).

Lanthanide Contraction

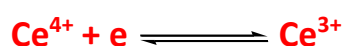
Each succeeding lanthanide differs from its immediate predecessor in having one or more electron in the 4f (though there are some exceptions) and an extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus force of attraction. This is due to the shape of f-orbitals. This led to a gradual increase in the attraction of the nucleus to the electrons in the outermost shell as the nuclear charge increases and not compensated by shielding effect, the result a consequent contraction in the atomic and ionic radius. In lanthanide contraction, the ionic radii of the lanthanides decrease progressively with increasing atomic number from lanthanum ($\text{La}^{3+}=1.06\text{\AA}$) to Lutetium ($\text{Lu}^{3+}=0.85\text{\AA}$) (see Table -1). As the ionic radii contract along the lanthanide series, the ability to form complex ions increase and this is the basis of their separation on an ion exchange column.

Cerric ammonium sulphate and its Analytical application

Cerric (IV) ammonium sulphate $(\text{NH}_4)_4[\text{Ce}(\text{SO}_4)_4] \cdot 2\text{H}_2\text{O}$: The IUPAC name of the compound is can be written as ammonium tetrasulphatocerrate (IV). It is prepared by the addition of ammonium sulphate to cerric (IV) sulphate solution. In order to prevent hydrolysis and crystallization, excess dilute H_2SO_4 should be added. This is powerful oxidizing agent, its reduction potential in 0.5 to 4.0 M H_2SO_4 at 25°C is $1.43 \pm 0.05\text{V}$. It can be used only acidic solution. 0.5M or higher concentration is best. The solution has intense yellow colour and in hot solution which are not dilute and end point may be detected without any indicator.

Analytical application: Application of cerium(IV) sulphate as a standard oxidizing agent are-

1. The Ce (IV) solutions are good strong oxidizing agents, so are used in redox titrations instead of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ in estimation of iron, copper, molybdate etc.
2. Cerium (IV) sulphate solution is remarkably stable for a long time and their concentration does not change on boiling or even in presence of light.
3. Cerium (IV) solution in 0.1M solution are not highly coloured to interfere vision when reading the meniscus in burette.
4. Cerium (IV) sulphate may be used in determination of reducing agent in the presence of high concentration of HCl. This is advantage over use of KMnO_4 in the same condition.
5. In the reaction of Ce (IV) salt in acid solution in the presence of reducing agent, the simple change



It is assumed to take place with permanganate ion, here a number of reduction product are produced. Solution of Ce (IV) in dil H_2SO_4 are stable even at boiling temperature. The aqueous Ce (IV) oxidizes concentrated HCl to Cl_2 . HCl solution of the salt are unstable because of reduction of Ce(IV) by the hydrochloric acid with the liberation of Cl_2 .



This reaction takes place rapidly on boiling and hence HCl can not be used in oxidation.

6. Ce (IV) is used as an oxidizing agent not only in titrimetric but they are also used in organic reactions like the oxidation of alcohols, aldehydes and

ketones at the alpha-carbon atom with the use of ceric ammonium sulphate solution.

Following ions are estimated with the use of ceric ammonium sulphate solution:



oxalate ion



nitrite ion



Iodide ion

Solution of Ce(IV) sulphate may be prepared by dissolving Ce (IV) sulphate or more soluble ammonium cerium (IV) sulphate in dilute H₂SO₄.

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Exercise

1. Name all the lanthanides and actinides and write down their electronic configuration and important chemical characteristics.
2. Discuss the chemistry of Lanthanide with respect to
 - (i) electronic configuration
 - (ii) oxidation state
3. What do you understand by f-block elements? Discuss electronic configuration and oxidation state of Lanthanide elements.
4. How are Lanthanide ions separated from each other. Give various method of separation.
5. What are Lanthanides and why are they called rare earth? Discuss their electronic configuration, magnetic properties and oxidation state.

6. What are Lanthanides and why are they so called? Discuss briefly the following properties of Lanthanides. (M.G.K.V.P-2012)

(i) Electronic configuration

(ii) Lanthanide contraction

(iii) Magnetic behaviour

(iv) Colour of tripositive ions

7. What are inner transition elements? Why these elements are called rare earth? Give the complex compounds and oxidation state of Lanthanides. (M.G. K. V. P.-2013)

8. What are Lanthanides? Write down their name, electronic configuration and variable oxidation states? (M.G.K.V.P.-2014)

9. Describe the extraction of Lanthanides from monazite sand.

Short Answer Questions

1. What are f-block elements? Where are they located in the periodic table?

2. What is Lanthanide contraction? How would you except for it?

3. Write the name of the important minerals containing Lanthanides.

4. How will you separate Lanthanides by ion-exchange method or modern method.

5. How can you separate Lanthanides with the method of change to oxidation state? (VBSPU-2011)

6. Discuss Lanthanide contraction and its consequences (MGKVP-2012).

7. Compare and contrast between Lanthanides and actinides.

8. Why it is difficult to separate Lanthanides from each other? Describe their separation by ion exchange method. (UP College-2018)

9. Describe horizontal similarity in Lanthanides and explain Lanthanide contraction? (UP College-2018)

10. Write extraction of Lanthanide. (MGKVP-2019)

11. Give the analytical application of ceric-ammonium sulphate.

12. Why is europium(III) more stable than cerium (II)?

Objective Questions

1. Which of the following Lanthanide ion is colourless?

(a) Lu^{3+}

(b) Tm^{3+}

(c) Sm^{3+}

(d) Nd^{3+}

2. The total number of elements present in f-block of periodic table are

(a) 28

(b) 20

(c) 35

(d) 30

3. The +3-oxidation state is the most stable for Lanthanide except-

- (a) Praseodymium (b) Terbium (c) Thulium
(d) Cerium

4. The elements belonging to 4f inner transition series are:

- (a) Pr, Th, Pu, Np, No (b) Sm, Pr, Th, Pu, Np
(c) La, Gd, Yb, Ce, Eu (d) Sm, Pr, Np, Cf, No

5. Which of the following is smallest in ionic size?

- (a) Dy^{3+} (b) Ce^{3+} (c) La^{3+}
(d) Lu^{3+}

6. Which of the following is diamagnetic?

- (a) Nd^{3+} (b) Pr^{3+} (c) La^{3+}
(d) Tm^{3+}

7. Which of the following has a stable +4 oxidation state?

- (a) Ce (b) La (c) Eu
(d) Gd

8. Which of the following does not belong to Lanthanide?

- (a) Pd (b) Eu (c) Nd
(d) Ce

9. The common oxidation state for all the Lanthanides is-

- (a) +4 (b) +5 (c) +3
(d) Ce

10. Main Smith colour sequence is associated with the colours of

- (a) tripositive actinide ions (b) tripositive lanthanide ions
(c) tetra positive lanthanide ions (d) dipositive lanthanide ions

Answers

1(a) 2(a) 3(d) 4(c) 5(d) 6(c) 7(a) 8(a) 9(c) 10(b)