

Some of the important properties of lanthanides are discussed below.

1. Electronic Configuration. We know that at ${}_{56}\text{Ba}$ 6s-orbital is completely filled (${}_{56}\text{Ba} \rightarrow [\text{Xe}] 6s^2$). In ${}_{57}\text{La}$ the incoming electron enters the 5d subshell and therefore it has the configuration $[\text{Xe}] 5d^1 6s^2 4f^0$. But after ${}_{57}\text{La}$ further filling of 5d-orbitals is discontinued. As the nuclear charge increases by one unit from ${}_{57}\text{La}$ to ${}_{58}\text{Ce}$, 4f-orbitals which were higher in energy up to ${}_{57}\text{La}$, fall slightly below the 5d level. 4f-orbitals, therefore, begin to fill and are completely filled upto ${}_{71}\text{Lu}$ before the filling of 5d-orbitals is resumed. Thus Ce has the configuration $[\text{Xe}] 6s^2 4f^1 5d^1$ and ytterbium has the configuration $[\text{Xe}] 6s^2 4f^{14} 5d^0$. At lutetium the electron enters the 5d subshell and it has the configuration $[\text{Xe}] 6s^2 4f^{14} 5d^1$.

The complete electronic configuration of lanthanides can be represented by a general configuration: $2, 8, 18, 4s^2 p^6 d^{10} f^{0, 2-14}, 5s^2 p^6 d^0 \text{ or } 1, 6s^2$ (including La) which shows that the valence-shell configuration can be represented as $f^{0, 2-14} 5d^0 \text{ or } 1 6s^2$.

The valence-shell configuration shows that the additional electron enters the d-orbitals without altering the electrons in the outmost 6s-orbital.

The filling 4f-orbitals is not regular, e.g., the additional electron in ${}_{64}\text{Gd}$ does not enter 4f-level but, instead, it goes to 5d-level. This is because the 4f and 5d orbitals in Gd are about the same energy level and Gd atom has a tendency to retain configuration with half-filled 4f-orbitals which are relatively more stable.

Oxidation States. The common oxidation state shown by all the lanthanides is +3. Some lanthanides also exhibit +2 and +4 oxidation states, but these are generally less stable than the group valency +3. It is possible to correlate the stability of various oxidation states of lanthanides with the electronic configuration of their ions. On the basis of general rule that empty, half-filled and completely filled orbitals are highly stable, thus the formation of Ce^{4+} , La^{3+} ($4f^0$), Tb^{4+} , Eu^{2+} , Yb^{2+} , Lu^{3+} ($4f^{14}$) ions can be explained. It is, however, difficult to explain the stability of oxidation states of the cations other than those given above. It may thus be assumed that in addition to the special stability associated with $4f^7$ and $4f^{14}$ configuration, there may be other factors such as thermodynamic kinetic, in determining the stability of various oxidation states of lanthanides.

The stability order of +2 oxidation state is $\text{Eu} > \text{Yb} > \text{Sm} > \text{Tm} \sim \text{Nd}$. LnI_2 solids (La, Ce, Pr and Gd) do not contain Ln^{2+} ions, but are metallic in nature. The stability of +4 oxidation state is $\text{Ce} > \text{Tb} \sim \text{Pr} > (\text{Nd} \sim \text{Dy})$.

Table 12.1 Electronic configuration and Oxidation states of lanthanides

Atomic number	Name	Symbol	Electronic configuration	Oxidation States
57	Lanthanum	La	[Xe] 4f ⁰ 5d ¹ 6s ²	+3
58	Cerium	Ce	[Xe] 4f ¹ 5d ¹ 6s ²	+3, +4
59	Praseodymium	Pr	[Xe] 4f ³ 5d ⁰ 6s ²	+3, +4
60	Neodymium	Nd	[Xe] 4f ⁴ 5d ⁰ 6s ²	+2, +3
61	Promethium	Pm	[Xe] 4f ⁵ 5d ⁰ 6s ²	+3
62	Samarium	Sm	[Xe] 4f ⁶ 5d ⁰ 6s ²	+2, +3
63	Europium	Eu	[Xe] 4f ⁷ 5d ⁰ 6s ²	+2, +3
64	Gadolinium	Gd	[Xe] 4f ⁷ 5d ¹ 6s ²	+3
65	Terbium	Tb	[Xe] 4f ⁹ 5d ⁰ 6s ²	+3, +4
66	Dysprosium	Dy	[Xe] 4f ¹⁰ 5d ⁰ 6s ²	+3, +4
67	Holmium	Ho	[Xe] 4f ¹¹ 5d ⁰ 6s ²	+3
68	Erbium	Er	[Xe] 4f ¹² 5d ⁰ 6s ²	+3
69	Thulium	Tm	[Xe] 4f ¹³ 5d ⁰ 6s ²	+2, +3
70	Ytterbium	Yb	[Xe] 4f ¹⁴ 5d ⁰ 6s ²	+2, +3
71	Lutetium	Lu	[Xe] 4f ¹⁴ 5d ¹ 6s ²	+3

3. Melting and boiling points. Lanthanides have fairly high melting and boiling points. However, their melting and boiling points do not show definite trend as we move from La to Lu. Both Eu and Yb form +2 ions and so it results in slightly weaker metallic bonding as there are fewer than three electrons per atom in the metallic bonding. As a consequence, melting and boiling points have lower values for these two elements as compared to the values for other lanthanide elements. Also abnormally greater radii for these two elements resulting in weaker packing account for lower melting and boiling points.

4. Metallic radii. The metallic radii decrease with increase in atomic number. The metallic radii of lanthanides fall in the range 174-208 pm which are quite comparable with those of s-block elements particularly Ca having metallic radius of 174pm. This indicates fairly large size of atoms of lanthanide elements. Eu and Yb show very surprisingly irregular sizes. The reason is that these elements suffer repulsions between greater number of f-electrons. Oxidation state of +2 for these elements is also responsible for anomalies.

5. Density. Lanthanides have low densities which range between 6.77 to 9.74g cm⁻³. However, densities of lanthanides do not show definite trend with rise in atomic number. Eu and Yb have low value of density than expected.

6. Ionization energies. Lanthanides have fairly low ionization energy values (IE₁ is about 585kJ/mol and IE₂ is about 1150 kJ/mol) due to their fairly large size which are quite comparable with those of alkaline earth metals particularly Ca (IE₁=589kJ/mol, IE₂ = 1145kJ/mol).

7. Electronegativity values. Their electronegativity values fall in the range 1.0-1.15 (Allred and Rochow scale) and are quite comparable with the electronegativity values of the *s*-block elements particularly Ca. Therefore, lanthanide ions are expected to form ionic compounds.

8. Atomic and ionic radii-Lanthanide contraction.

As we move along the lanthanide series from La to Lu, there is a continuous decrease in atomic and ionic radii. This steady decrease in the atomic and ionic radii of lanthanide with increase in atomic number is called **lanthanide contraction**. The decrease in size is regular in ions but not so regular in case of atoms.

Cause of lanthanide contraction. In lanthanides the additional electron enters *4f*-subshell but not in the valence shell namely sixth shell. The shielding effect of one electron in *4f*-subshell by another in the same shell (i.e. mutual shielding effect of *4f*-electrons) is very little (poor), being even smaller than that of *d*-electrons, because the shape of *f* orbitals is very much diffused. The nuclear charge (i.e. At. no) however, increase by one unit at each step. Thus the nuclear charge increases at each step, while there is no comparable increase in the mutual shielding effect of *4f*-electrons. This results is that electrons in the outmost shell experience increasing nuclear charge from the growing nucleus. Consequently the atomic and ionic radii go on decreasing as we move from $_{57}\text{La}$ to $_{71}\text{Lu}$.

Consequences of lanthanide Contraction

(i) **Electronegativity.** There is a slight increase in electronegativity of trivalent ions.

(ii) **Ionic radius.** There is steady decrease in the ionic size.

(iii) **Basic character of lanthanide oxides, Ln_2O_3 and hydroxides, $\text{Ln}(\text{OH})_3$.**

There is a decrease in basic strength of the oxides and hydroxides of lanthanides with increase in atomic number. Thus $\text{La}(\text{OH})_3$ is the *most basic* while $\text{Lu}(\text{OH})_3$ is the *least basic*. Due to lanthanide contraction the decrease in the size of Ln^{3+} cations increases the covalent character (i.e. decreases the ionic character) between the lanthanide ion (Ln^{3+} ion) and the OH^- ion (according to Fajan's rules), thereby reducing the basic character of the lanthanide oxides and hydroxides. Basicity decreases as the ionic radius decreases.

(iv) **Atomic and ionic radii of post-lanthanide elements.** The elements following lanthanides are called *post-lanthanide elements*. Normally in the same sub-group, the covalent radii increases as the atomic number increases. This fact is evident when we compare the covalent radii values of the elements of the first and second transition series.

If we compare the covalent radii values of the elements of the second transition series with those of the third transition series, we find that the

increase in the covalent radii values from ${}_{21}\text{Sc}$ to ${}_{39}\text{Y}$ to ${}_{57}\text{La}$ disappears after lanthanides and the pairs of elements: Zr-Hf, Nb-Ta....., Ag-Au, Cd-Hg possess almost same values. If the fourteen lanthanides had not been intervened between ${}_{57}\text{La}$ and ${}_{72}\text{Hf}$, the value of covalent radius, for example, of Hf should have been greater than that of ${}_{40}\text{Zr}$ since Zr and Hf both are in the same sub-group IVB (Group 4) and Zr lies immediately above Hf.

The occurrence of lanthanide contraction cancels the expected increase in the covalent radius value from Zr to Hf. This situation is also with other pairs of elements in the second and third series of transition elements. Since the pairs of elements of second and third transition series, occurring after lanthanides, (e.g. Zr-Hf, Nb-Ta etc pairs) have almost similar size (which is due to lanthanide contraction), they are much close to one another in properties than do the pairs of elements of first and second transition series.

Table. 12.2 Atomic (covalent) radii (in Å°) of the elements preceding and following Lanthanides

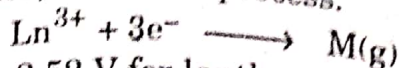
Transition Series	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	
First	${}_{21}\text{Sc}$ 1.44	Ti 1.32	V 1.22	Cr 1.18	Mn 1.17	Fe 1.17	Co 1.16	Ni 1.15	Cu 1.17	Zn 1.25	
Second	${}_{39}\text{Y}$ 1.62	Zr 1.45	Nb 1.34	Mo 1.30	Tc 1.27	Ru 1.25	Rh 1.25	Pd 1.28	Ag 1.34	Cd 1.48	
Third	${}_{57}\text{La}$ 1.69	Ce-Lu 1.65-1.56 14 Lanthanides	Hf 1.44	Tb 1.34	W 1.30	Re 1.28	Os 1.26	Ir 1.27	Pt 1.30	Au 1.34	Hg 1.49

(v) **High density of post-lanthanide elements.** Because of lanthanide contraction the atomic sizes of the post-lanthanide elements become very small. Consequently the packing of atoms in their metallic crystals become so much compact that their densities are very high. Thus, while the densities of the elements of second transition series are only slightly higher than those of first transition series, the densities of the elements of third transition series are almost double to those of elements of second transition series.

(vi) **Occurrence of Y with heavy lanthanides.** The crystal radii of Y^{3+} and Er^{3+} are equal ($\text{Y}^{3+} = 0.93\text{Å}^\circ$ and $\text{Er}^{3+} = 0.96\text{Å}^\circ$). This similarity in ionic size of these two cations coupled with the equality in ionic charge ($= +3$ in both the ions) accounts for the invariable occurrence of Y with heavier lanthanides. The marked similarities in the crystal structure, chemical properties and solubility between yttrium compounds and the corresponding ones of the heavier lanthanides make it difficult to separate yttrium from the heavier lanthanides. It is because of these similarities that yttrium is regarded for all practical purposes as member of lanthanide series.

ii) **E° value.** There is a small but smooth increase in standard electrode

potential values, E° for the process.



ranging from -2.52 V for lanthanum to -2.25 V for lutetium.

9. Colour and absorption spectra. The lanthanide metals are silvery white but some of the trivalent lanthanide (Ln^{3+}) ions are coloured in the solid and in aqueous solution. Colour of the ions depends on the number of unpaired electrons because the Ln^{3+} cations containing x electrons in $4f$ -level have the same colour as the Ln^{3+} cations containing $(14-x)$ electrons in the $4f$ -orbital, e.g., Pr^{3+} and Tm^{3+} ions having 2 and $(14-2)$ i.e., 12 electrons in the $4f$ -orbital respectively have the same colour namely green.

The colour of lanthanide ions is due to the presence of partly filled *f*-orbitals. As a result it is possible to absorb certain wavelength from the visible region of the spectrum. The results in transition from one $4f$ -orbital to another $4f$ -orbital known as *f-f* transition. The colour one sees is the result of absorption of light of certain wavelengths and transmission of light of other wavelengths.

Ln^{3+} ions having empty, half-filled or completely filled $4f$ -orbitals (i.e., $4f^0$, $4f^7$ and $4f^{14}$ configuration) are colourless, e.g., La^{3+} ($4f^0$), Gd^{3+} ($4f^7$) and Lu^{3+} ($4f^{14}$) ions are colourless.

Since the colour is due to the absorption of light by the cations in the visible region of the spectrum, it seems that the bands in the absorption spectra are due to the transition of the electrons from one level to the other within the $4f$ -level, i.e., due to *f-f* transition. The absorption spectra of the Ln^{3+} ions show very sharp linelike bands in the ultraviolet, visible or near infrared regions. The bands of Ln^{3+} ions are so sharp that they are very useful for characterising the lanthanides and for their quantitative estimations.

10. Magnetic Properties. Magnetism is a property associated with unpaired electrons. All lanthanide ions (Ln^{3+} ions) with the exception of La^{3+} , Lu^{3+} , Yb^{3+} and Ce^{4+} are paramagnetic because they contain unpaired electrons in the $4f$ orbital. Their magnetic moment do not obey the simple "spin only" formula (except for $4f^0$, $4f^7$ and $4f^{14}$ cases) for the magnetic moment.

$$\sqrt{\mu \text{ spin only}} = \sqrt{n(n+2)} \text{ where } n \text{ is equal to the number of unpaired electrons.}$$

In case of lanthanides, the magnetic effect arising from the orbital motion of the electron as well as that arising from the electrons spinning on its axis, contributes to the total magnetic moment. Therefore, magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions and a more complex formula.

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

which involves the orbital quantum number, L and spin quantum number, S is used.

Magnetic moment values of lanthanides vary depending upon the atomic number. Lu^{3+} is diamagnetic (due to f^0) and the value of magnetic moment increases attaining maximum value at neodymium. It then suddenly drops to 1.47

for samarium. It increases again reaching maximum value for dysprosium and holmium. Thereafter, it again falls touching zero at lutetium which is diamagnetic because it contains 14 electrons in its f orbitals.

12.3 Chemical properties of lanthanides

In general, the lanthanides behave as active metals. Their electrode potential values are comparable to those of alkaline earth metals. All the metals act as strong reducing agents.

(i) **Action with acids.** All lanthanides are attacked by acids with the liberation of hydrogen.

(ii) **Action with water.** The standard electrode potential values, E° indicate that these metals should react vigorously with water. In fact they do liberate hydrogen slowly from cold water and rapidly from hot water.

(iii) **Action with air.** They are easily tarnished in moist air. If ignited in air they burn to give 3+ and 4+ oxides like Ln_2O_3 or CeO_2 .

(iv) **Action with nitrogen.** They react with nitrogen to form metal nitrides of the general formula MN .

(v) **Action with halogen.** They combine directly with halogens to give trihalides MX_3 .

(vi) **Action with hydrogen.** They react with hydrogen especially at elevated temperature and form non-stoichiometric hydrides having composition MH_2 and MH_3 .

(vii) **Formation of complexes.** Although the lanthanide ions have a high charge (+3), yet the size of their ions is very large (yielding small charge to size ratio). As a consequence they have poor tendency to form complexes. They form complexes mainly with chelating agents such as β -diketones, EDTA, β -hydroxyquinoline, oxalic acid, ethylenediamine, etc.

(viii) **Reaction with anions.** Nearly all known anions form the compounds with Ln^{3+} cation. These compounds are stable in solid as well as in solution state. Compounds of Ln^{3+} cation with the anions such as OH^- , CO_3^{2-} , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, NO_3^- etc decompose on heating, give first basic salts and finally oxides. Hydrated salts that contain thermally stable anions such as F^- , Cl^- , Br^- , PO_4^{3-} etc also give similar products on heating because of hydrolysis.

Compounds of Ln^{3+} cation with the anions Cl^- , Br^- , I^- , NO_3^- , CH_3COO^- , BO_3^{3-} are generally soluble in water while those with F^- , OH^- , O^{2-} , $\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , PO_4^{3-} are generally insoluble in water.

12.4 Occurrence of Lanthanides

Each lanthanide mineral contains all lanthanides although some in traces only, excepting Pm which is an unstable radioactive element. The important minerals of lanthanides are as follows:

(i) **Monazite sand** which contains predominantly the mixture of phosphates of light lanthanides (i.e., ${}_{57}\text{La}$ to ${}_{63}\text{Eu}$). Its approximate composition is: light lanthanides 50-70%, heavy lanthanides (i.e., ${}_{64}\text{Gd}$ to ${}_{71}\text{Lu}$) 1-4%, ThO_2 5-10%, SiO_2 1-2%, P_2O_5 22-30%, traces of uranium, ZrO_2 , TiO_2 etc.

(ii) **Xenotime** which contains predominantly the mixture of phosphates of heavy metals. It is analogous to Monazite and has the approximate composition as: heavy lanthanides 54-65%, light lanthanides ~0.1%, ThO_2 3%, U_3O_8 3.5%, ZrO_2 2-3%.

12.5 Extraction of Lanthanides from Monazite mineral

Lanthanides are mainly extracted from monazite mineral which chiefly worked for thorium and the lanthanides are obtained as by products. The operation consists of the following three steps.

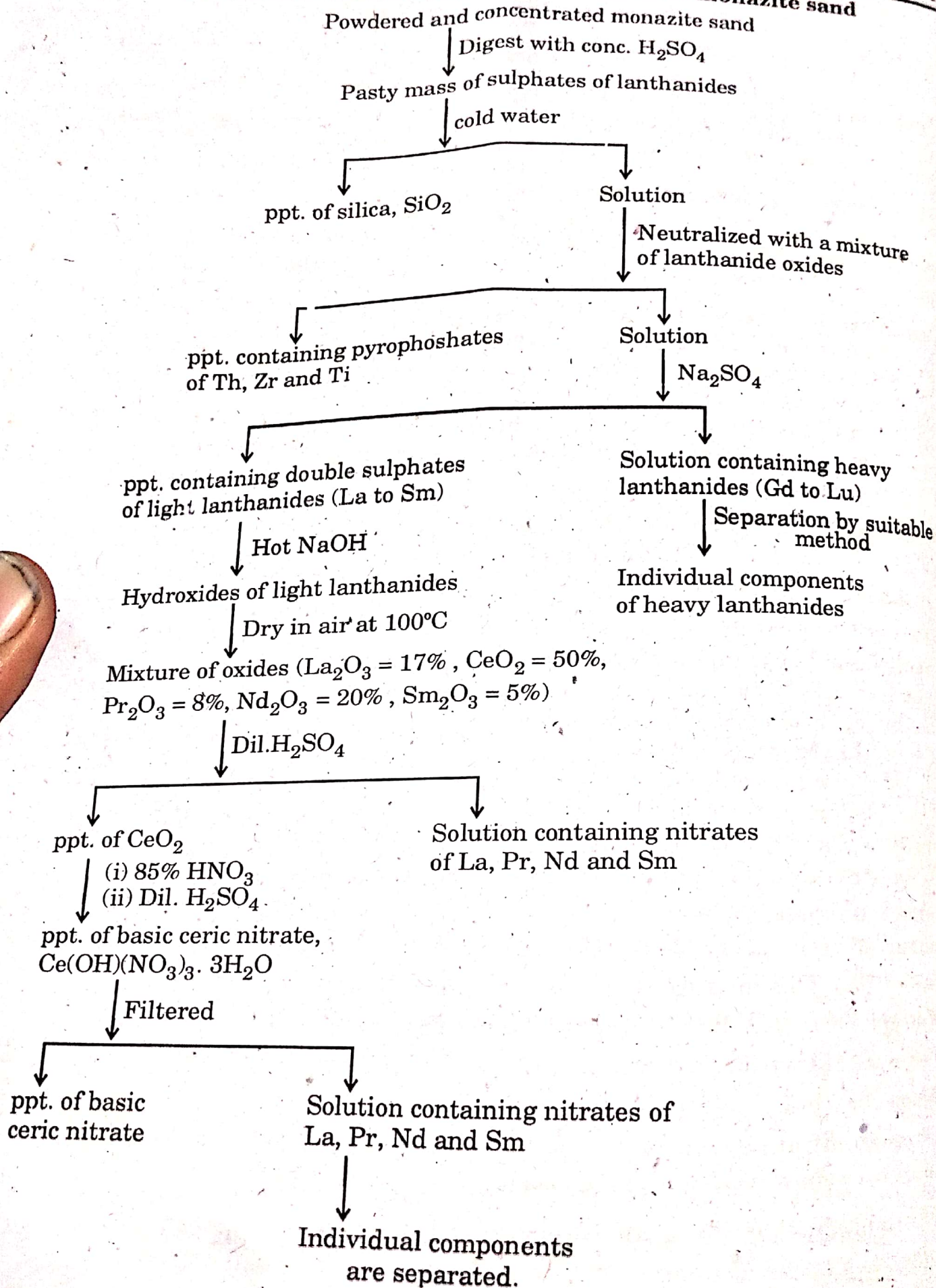
(i) **Concentration of the mineral.** The concentration of monazite sand is usually begun with gravity separation on Wilfley tables. Since monazite sand is much more heavier than quartz, the monazite sand gets caught up on the riffles and the quartz sand and other gangue material is washed off. The heavy material which contains monazite sand and other material sands is dried and then passed through magnetic separator. The monazite, being much less magnetic than the other material sand, gets thereby separated from the rest.

(ii) **Cracking of the mineral.** The finely powdered and concentrated monazite mineral is digested with concentrated H_2SO_4 until a paste of lanthanide sulphates containing phosphoric acid (formed by the reaction of P_2O_5 with H_2O), and excess of H_2SO_4 , is formed. The paste is centrifuged and then treated with cold water when silica being insoluble precipitates out. The solution is neutralized with a mixture of lanthanide oxides when thorium, zirconium and titanium precipitate out as pyrophosphates. Sodium sulphate is added to the clear mother liquor so that light lanthanides (La to Sm) may precipitate out as double salts while the heavy lanthanides (Gd to Lu) still remain in solution.

Hot sodium hydroxide is added to precipitate double sulphates of light lanthanides to form a mixture of hydrated oxides. This is washed (till free from Na_2SO_4) and dried in air at 100°C where by cerium is completely oxidized to CeO_2 while other lanthanides change into their oxides. At this stage, the approximate composition of residual solids is CeO_2 (50%), Nd_2O_3 (20%), La_2O_3 (17%), Pr_2O_3 (8%), Sm_2O_3 (5%). This mixture is treated with dilute HNO_3 when all the lanthanide oxides (except CeO_2) get dissolved and filtered. The crude CeO_2 is dissolved in 85% HNO_3 and cerium is precipitated from it as the red basic nitrate, $\text{Ce}(\text{OH})(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ by the addition of excess of dilute H_2SO_4 . The solution obtained after removing cerium as basic cerium nitrate contains the nitrates of La, Pr, Nd and Sm. The individual lanthanides are separated from this solution by suitable methods.

The solution containing the sulphates of heavy lanthanides can also be used to separate the individual components by different methods discussed below:

Flow Sheet. Extraction of lanthanides from monazite sand



12.6 Separation of Lanthanide elements

1. **Old Classical methods.** The following classical methods were not only used by the early chemists in the past, but still remain as very important methods for economical production of lanthanides on commercial scale.

(i) **Fractional crystallization.** This procedure depends on slight difference in the solubility of various salts. The simple salts of lanthanides like nitrates, sulphates, oxalates, bromates and double salts such as $2\text{Ln}(\text{NO}_3)_3 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, $2\text{Ln}(\text{NO}_3)_3 \cdot 3\text{Mn}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$, $\text{Ln}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, etc are utilized in this procedure. Since the solubility of these simple and double salts decreases from La to Lu, these lanthanides can be separated from each other by repeating the fractional crystallization a number of times as follows.

The mixed solution of lanthanide salts is evaporated to such an extent that, if it is allowed to cool, it would deposit about one-half of the dissolved salts of crystals.

The crystal obtained as result of first evaporation are redissolved in just sufficient amount of water and the solution is evaporated as before to such an extent that on cooling, it would deposit one-half of the dissolved salts as crystals. Similarly, the liquor from the first crystallization is also evaporated further so that one-half of the dissolved salt may be obtained as crystals.

The crystals and mother liquors obtained from the second set of operations are separated from each other, and the mother liquor from the first crystallization is combined with the crystals from the second evaporation of the original mother liquor. The starting solution thus get separated, at this stage into three fractions:

The three fractions are then submitted to crystallization as before and the resulting liquors are combined with crystal from adjacent solution. The four fractions which thus result, on being processed in the same way as before, give rise to five fractions. Each series of operations, therefore, gives one more fraction.

As a result of the repetition of the above process, the components which are less soluble continuously pass on to the crop of crystals, while those which are soluble pass to the final mother liquor. The process is continued, until the desired degree of separation has been achieved. The systematic fractional crystallization of any given mixture of lanthanides results in the separation into:

- The least soluble components that accumulate more and more in each successive crop of crystals.
- The more soluble components that progressively accumulate in the mother liquor.
- The intermediate components, distributed between the final crop of crystal and the end mother liquor, in the order of solubility.

(ii) **Fractional precipitation method.** It has already pointed out that the basic character of the hydroxides of lanthanide elements decreases from La_{57} to Lu_{71} . Thus the hydroxides of light lanthanide elements ($\text{La}_{57} - \text{Eu}_{63}$) are more basic than those of heavy lanthanides ($\text{Gd}_{64} - \text{Lu}_{71}$). When pH of the solution containing mixture of the lanthanide

elements is gradually increased by adding NH_3 , amine or alkali etc, the hydroxides of heavy lanthanides being less basic get preferentially precipitated while those of light lanthanides which are more basic are left behind in the solution. From a given sub-group individual lanthanides are then separated by the further fractional precipitation of the hydroxides, Since the basicity differences in the hydroxides of lanthanide elements are small, complete separation of the adjacent members in a given sub-group by this method of fractional precipitation cannot be made.

(iii) **Change of oxidation state by selective oxidation or reduction.** As already mentioned, some of the lanthanides show +2 and +4 oxidation states in addition to +3 oxidation state which is the common state for all the lanthanides. The properties of Ln^{2+} and Ln^{4+} ions are different from those of the Ln^{3+} ions. A change in oxidation state results in a remarkable change in properties. Selective oxidation or reduction, therefore, provides a very effective method of separating specific lanthanides.

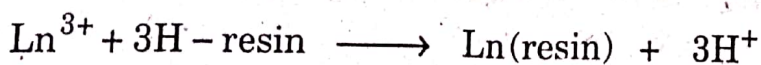
Examples: (i) Suppose we have to separate Ce from a mixture containing Ce^{3+} and other trivalent lanthanide cations. This mixture is treated with some strong oxidizing agent such as bromate in neutral medium or chlorine or KMnO_4 in alkaline medium. By this treatment only Ce^{3+} ion is oxidized to Ce^{4+} ion while other lanthanide ions remain as Ln^{3+} ions. Since Ce^{4+} ion is smaller than Ce^{3+} ion, Ce^{4+} ion is less basic and less soluble. Ce^{4+} ion can thus be precipitated as $\text{Ce}(\text{OH})_4$ by the addition of a small amount of an alkali leaving all other Ln^{3+} ions in solution. By this method it has been possible to have 99% pure Ce from a mixture containing only 40% Ce.

(ii) Eu^{3+} can almost quantitatively be separated from a solution containing Eu^{3+} and other Ln^{3+} ions by reducing it to Eu^{2+} by means of Zn-amalgam and then precipitating it as EuSO_4 which is insoluble in water and hence can be separated, while the sulphates of all the trivalent lanthanides are soluble in water.

2. Modern Methods. Following are the modern methods which are now used for separating individual lanthanides.

(i) **Ion-exchange method.** This is the most rapid and effective method for the separation and purification of the lanthanides. This method is based on the following principles.

(i) Lanthanide ions on contact with synthetic resins containing $-\text{COOH}$ group or $-\text{SO}_3\text{H}$ group undergo proton exchange.



(ii) π bonding of the lanthanide ion to the resin depends on its size, i.e., the smaller the size of the lanthanide ion, the more firmly it is bound to the resin and vice-versa. Since lanthanide ions are hydrated, therefore size of the hydrated ions should be considered for binding purpose. Hydration of the ions depends upon size i.e., smaller the size of the ion