

Study material for B.Sc Chemistry (Honours) Sem-4

CEMA-CC-4-10-TH (Inorganic Chemistry-4)

LANTHANOIDS AND ACTINOIDS

CHEMISTRY OF THE LANTHANIDE ELEMENTS

Lanthanides are the elements which constitute a distinct series of fourteen elements from cerium (Ce, $Z = 58$) to lutetium (Lu, $Z = 71$). They are so called because these elements succeed lanthanum (La, $Z = 57$), the element of Group 3 and lie between it and hafnium (Hf, $Z = 72$), the element of Group 4, both belonging to third transition series (or 5d-transition series). That is why they are also known as inner transition elements. These fourteen elements belong to f-block and are the members of 4f-series because the last or differentiating electron in the atoms of these elements enters 4f-subshell, i.e., the f-subshell of ante-penultimate shell (here $n=6$). Thus, f-block elements have partly filled f-subshells of $(n-2)$ th shell in the elementary or ionic state.

The first and the last elements of the 4f-series have been mentioned above (i.e., Ce and Lu).

The rest twelve elements along with their symbols and atomic numbers are given below:

praseodymium (Pr, $Z = 59$), neodymium (Nd, $Z = 60$), promethium (Pm, $Z = 61$), samarium (Sm, $Z = 62$), europium (Eu, $Z = 63$), gadolinium (Gd, $Z = 64$), terbium (Tb, $Z = 65$), dysprosium (Dy, $Z = 66$), holmium (Ho, $Z = 67$), erbium (Er, $Z = 68$), thulium (Tm, $Z = 69$) and ytterbium (Yb, $Z = 70$). In analogy with various series of d-block elements, these elements are called first inner transition series elements. All the fourteen elements of the series resemble closely in their electronic configuration and chemical properties with one another as well as with lanthanum which may be called a prototype of lanthanide elements. All these elements said to be the members of Group 3, i.e., Sc group and have been allotted one single position in the periodic table.

These elements were originally called rare earth elements because the elements then known occurred as oxides (earths) and were available scarcely. All the elements have similar physical and chemical properties hence are considered together for their study.

It is interesting to note that the elements with even atomic numbers are relatively more abundant and also have a larger number of isotopes but those with odd atomic numbers are less abundant and do not have more than two isotopes. Promethium ($Z = 61$) has been made artificially only and does not occur in nature.

Electronic configuration

The electronic configurations of the lanthanides have been derived from the electronic spectra of the atoms of these elements. These spectra have great complexity thereby inferring to some doubt about the configurations. In the following table, the expected and alternative probable configurations of the elements have been listed. The expected configurations have been derived by taking into account the electronic configuration of lanthanum and supposing that in all the lanthanide elements succeeding lanthanum, additional electrons are filled in 4f-subshell successively from cerium to lutetium. Thus, the 4f-electrons are embedded in the interior while 5d and 6s electrons are exposed to the surroundings. The electronic configurations of lanthanide elements are given in Table below:

Table: Electronic structures of lanthanum and lanthanides

Element	Atomic number (Z)	Electronic Configuration of outer orbital	
		Ln	Ln ³⁺
Lanthanum (La)	57	4f ⁰ 5d ¹ 6s ²	4f ⁰
Cerium (Ce)	58	4f ¹ 5d ¹ 6s ²	4f ¹
Praseodymium (Pr)	59	4f ³ 6s ²	4f ²
Neodymium (Nd)	60	4f ⁴ 6s ²	4f ³
Promethium (Pm)	61	4f ⁵ 6s ²	4f ⁴
Samarium (Sm)	62	4f ⁶ 6s ²	4f ⁵
Europium (Eu)	63	4f ⁷ 6s ²	4f ⁶
Gadolinium (Gd)	64	4f ⁷ 5d ¹ 6s ²	4f ⁷
Terbium (Tb)	65	4f ⁹ 6s ²	4f ⁸
Dysprosium (Dy)	66	4f ¹⁰ 6s ²	4f ⁹
Holmium (Ho)	67	4f ¹¹ 6s ²	4f ¹⁰
Erbium (Er)	68	4f ¹² 6s ²	4f ¹¹
Thulium (Tm)	69	4f ¹³ 6s ²	4f ¹²
Ytterbium (Yb)	70	4f ¹⁴ 6s ²	4f ¹³
Lutetium (Lu)	71	4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴

According to the latter view, as is evident from the table, the solitary 5d electron shifts into the 4f-subshell in all the cases except in Gd (64) and Lu (71) because it is favourable energetically to move the single 5d-electron into 4f-orbital in most of the elements and give more appropriate electronic configuration which is widely accepted. In Gd such a shift would have destroyed the symmetry of a half-filled f-subshell and the resulting configuration would have been less stable than the probable configuration i.e., 4f⁷ is more stable than 4f⁸ configuration. In lutetium, the f-subshell is already completely filled and cannot accommodate any additional electron.

From the above, it may be concluded that the general electronic configuration of lanthanide elements could be written as [Xe](n-2)f¹⁻¹⁴(n-1)d⁰1ns² where n is the principal quantum number, i.e., 6. The three subshells, viz., (n-2)f, (n-1)d and ns together form the valence shell of these elements, i.e., 4f.5d.6s = valence shell.

Oxidation states

It has been shown that the lanthanide elements are highly electropositive and form essentially ionic compounds. It is observed for these elements that +3 (i.e. formation of tripositive ions, Ln^{3+}) is the principal or common oxidation state exhibited by all of them. This is said to be the most stable oxidation state of the lanthanides. Some of these elements also show +2 and +4 oxidation states but except a few such ions, they have the tendency to get converted to +3 state. For example, Sm and Ce form Sm^{2+} and Ce^{4+} ions but are easily converted to +3 states. That is why Sm^{2+} is a good reducing agent while Ce^{4+} is a good oxidising agent, i.e.,



It means Ln^{2+} and Ln^{4+} ions are less frequent than Ln^{3+} ions among the lanthanides.

+2 and +4 oxidation states are shown by the elements particularly when they lead to:

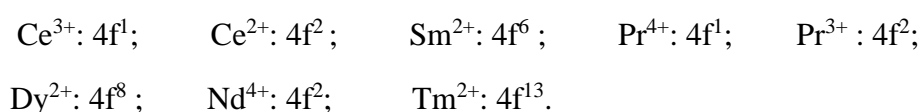
(a) Noble gas electronic configuration, e.g., Ce^{4+} ($4f^0$),

(b) Half-filled f-orbital, e.g., Eu^{2+} and Tb^{4+} ($4f^7$), and

(c) Completely filled f-orbital, e.g., Yb^{2+} ($4f^{14}$) in the valence shell.

Among the above, +2 and +4 oxidation states, which exist only in aqueous solutions, are exemplified by Sm^{2+} , Eu^{2+} , Yb^{2+} and Ce^{4+} .

There are some exceptions also, i.e., sometimes +2 and +4 oxidation states are also shown by the elements which are close to f^0 , f^7 and f^{14} states, e.g., the valence shell configurations of the ions given below are $4f^1$, $4f^2$, $4f^3$, $4f^6$ and $4f^8$, etc.:



No satisfactory explanation for these exceptions has yet been given. These oxidation states have only been explained on the basis of thermodynamic and kinetic factors, that too arbitrarily. Due to the only one stable oxidation state (i.e., +3), lanthanide elements resemble each other much more than do the transition (or d-block) elements. It has also been observed that the higher oxidation states of the lanthanides are stabilized by fluoride or oxide ions, while the lower oxidation states are favoured by bromide or iodide ions. Among the lanthanides, in addition to +3 states, +2 states is shown by Nd, Sm, Eu, Tm, and Yb only whereas +4 state is exhibited by Ce, Pr, Nd, Tb and Dy elements. Rest five elements show only +3 states.

Colour and Spectral properties

Lanthanide ions are weakly coloured. The spectra of their complexes show much narrower and more distinct absorption bands which is associated with weak f-f transition. The 4f orbital are deeply embedded inside the atom and well shielded by 5s and 5p electrons. The f electrons are practically unaffected by complex formation; hence colour remains almost constant for a particular ion regardless of the ligands (see Table below). The bands due to f-f transition are sharp compared to the broad bands for d-d transition. Absorption bands due to 4f-5d transitions are broad and are affected by ligand environment.

All lanthanoid ions (except La^{3+} (f^0) and Lu^{3+} (f^{14}) show luminescence Eu^{3+} (f^6) and Tb^{3+} (f^8) showing particularly strong emissions. This has been attributed to the large number of excited states that exist which decays to the ground state with either emission of energy (fluorescence) or non-radiative pathways. The origin of this is f-f transition. The luminescence of lanthanoid complexes is the reason they are used as phosphors on TV screens and fluorescent lighting.

Ions	No. of 4f electrons	Colour
La ³⁺	4f ⁰	Colourless
Ce ³⁺	4f ¹	Colourless
Pr ³⁺	4f ²	Green
Nd ³⁺	4f ³	Lilac
Pm ³⁺	4f ⁴	Pink
Sm ³⁺	4f ⁵	Yellow
Eu ³⁺	4f ⁶	Pale pink
Gd ³⁺	4f ⁷	Colourless
Tb ³⁺	4f ⁸	Pale pink
Dy ³⁺	4f ⁹	Yellow
Ho ³⁺	4f ¹⁰	Pink
Er ³⁺	4f ¹¹	Lilac
Tm ³⁺	4f ¹²	Green
Yb ³⁺	4f ¹³	Colourless
Lu ³⁺	4f ¹⁴	Colourless
Ce ⁴⁺	4f ⁰	Orange-red (Isoelectronic La ³⁺ Colourless)
Sm ²⁺	4f ⁶	Yellow (Isoelectronic Eu ³⁺ Pale pink)
Eu ²⁺	4f ⁷	Pale greenish yellow (Isoelectronic Gd ³⁺ colourless)
Yb ²⁺	4f ¹⁴	Colourless (Isoelectronic Lu ³⁺ Colourless)

Magnetic properties

Magnetism is a property associated with unpaired electrons. La³⁺ (f⁰), Ce⁴⁺ (f⁰), Yb²⁺ (f¹⁴) and Lu³⁺ (f¹⁴) have no unpaired electron, hence they are diamagnetic. Other lanthanide ions have unpaired electron in 4f orbital, so they are paramagnetic.

Magnetic behaviour in case of lanthanides arises due to the contribution of both spin moment as well as orbital magnetic moment, unlike the d-block elements where magnetic moment corresponds to spin only values [$\mu = \sqrt{n(n+2)}$, n = no. of unpaired electrons]. Because in case of inner-transition f-block elements, the 4f orbitals are quite shielded from the surroundings

and do not interact strongly with the ligands surrounding the metal ion. Consequently, the orbital motion of 4f orbitals are not restricted (not quenched). Therefore, 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: $\mu = \sqrt{4S(S+1) + L(L+1)}$ is used, where L = orbital quantum no. and S = spin quantum no.

In case of lanthanides, the spin contribution (S) and orbital contribution (L) couple together to give a new quantum no. J, called total angular momentum quantum no.

$$J = L - S, \text{ when the orbital is less than half full}$$

$$J = L + S, \text{ when the orbital is more than half full}$$

Magnetic moment values for lanthanides in Bohr Magneton (BM) is given by:

$$\mu = g\sqrt{J(J+1)}$$

Where g is called Lande splitting factor and is given by:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Lanthanide contraction

Here, ionic radii of tripositive ions (i.e., Ln^{3+}) have only been considered because +3 is the most stable and common oxidation state of all the lanthanides, in general. It has been observed that the atomic as well as the ionic radii of lanthanides decrease steadily as we move from Ce to Lu. The ionic radii have been listed below (for Ln^{3+} ions):

Ln ³⁺ ions	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⁺
Ionic radii (pm)	103	101	100	98	96	95	94	92	91	90	89	88	86	85

From the above list it is clear that the ionic radii decrease steadily all along the series amounting in all to 18 pm. This shrinking in the ionic size of the Ln³⁺ ions with increasing atomic number is called lanthanide contraction. The term steadily decrease means the values decrease regularly and with a very small difference though the nuclear charge increases by +14 units from the first to the last element.

The atomic radii of these elements also decrease from Ce to Lu (Ce : 165 pm, Lu : 156 pm) but the overall shift is only of 165-156 = 9 pm. These values do not decrease regularly like ionic radii rather there are some irregularities at Eu and Yb which have abnormally high atomic radii. (Eu : 185 pm, Yb : 170 pm).

The atomic radii for the metals are actually the metallic radii which are recorded for the metal atoms surrounded by 8 or 12 nearest neighbours (in bulk). Various metal atoms in metal crystal are bonded together by metallic bonding. In Eu and Yb, only two 6s-electrons participate in metallic bonding, 4f-subshells being stable. For other lanthanides, three electrons are generally available for this purpose. This results in larger atomic volumes for Eu and Yb because of weaker bonding among atoms. The larger values ultimately give rise to the larger size to the atoms of the elements.

Cause of Lanthanide Contraction

As we move along the lanthanide series from Ce to Lu, the addition of electrons takes place to the 4f-orbitals, one at each step. The mutual shielding effect of f-electrons is very little, being

even smaller than that of d-electrons, due to the scattered or diffused shape of these orbitals. However, the nuclear charge (i.e. atomic number) goes on increasing by one unit at each step (i.e., each next element). Thus, the attraction between the nucleus and the outermost shell electrons also goes on increasing gradually at each step. The 4f-electrons are not able to shield effectively the attraction of the nucleus (i.e. inward pull) for the electrons in the outer most shell as the atomic number of lanthanide elements increases. This results in the increased inward pull of the outer most electrons by the nucleus, finally causing the reduction in the atomic or ionic size of these elements. The sum of the successive reductions gives the total lanthanide contraction.

It may be concluded that the lanthanide contraction among the 4f-series elements and their ions takes place due to the poor shielding effect of 4f-electrons and gradual increase in the nuclear charge.

Consequences of Lanthanide Contraction

Lanthanide contraction plays an important role in determining the chemistry of lanthanides and heavier transition series elements. Some important consequences of lanthanide contraction are discussed below:

(a) Basic character of lanthanide hydroxides, $\text{Ln}(\text{OH})_3$:

Because the size of tripositive lanthanide ions (Ln^{3+}) decreases regularly with increasing atomic number (or nuclear charge), the process being called lanthanide contraction, therefore, the covalent character between Ln^{3+} ion and OH^- ions increases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$ (Fajans' rules). As a result, the basic character of the hydroxides decreases with increasing atomic number. Consequently, $\text{La}(\text{OH})_3$ is the most basic while $\text{Lu}(\text{OH})_3$ is the least basic.

(b) Resemblance between the atomic radii of the second and third transition series elements:

The lanthanide contraction is an important factor in allowing the separation of lanthanides from one another. Also, it has significant effect on the relative properties of the elements which precede and succeed the lanthanides. Normally in the same group, the atomic (or covalent) radii increase as the value of n (principal quantum number) increases due to increased distance between the nucleus and the outermost shell of the electrons which counterbalances the increased nuclear charge. This fact is evident when the values of atomic radii are compared for the elements of first and second transition series. On the same analogy, the atomic radii of the elements of third transition series should be greater than those of the second transition series elements. This statement is valid only for the elements of Group 3, i.e. Sc, Y and La in terms of their atomic radii (see the table given below). But, when these values are compared for the elements of 4d and 5d series in the next group, viz. Group 4, 512, it is observed that the values are unexpectedly almost equal. The similarity in the values of atomic radii for the elements of second and third transition series is attributed to the inclusion of 14 lanthanides between La ($Z = 57$, Group 3) and Hf ($Z = 72$, Group 4) of third transition series which due to “lanthanide contraction” cancel the increase in the values of atomic radii. Due to the similarity in the size of the elements of the two series (i.e., second and third), the elements of a particular Group resemble each other more closely in their properties than do the elements of first and second transition series. The examples of the pairs of elements which show similar properties and hence are difficult to separate are Zr- Hf, Nb-Ta, Mo-W, Ru-Os, Rh-Ir, Pd-Pt and Ag-Au. The atomic radii of the elements of the three transition series are given below to justify the above statement.

Groups	3	4	5	6	7	8	9	10	11	12
Elements of 3d series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii (pm)	144	132	122	117	117	117	116	115	117	125
Elements of 4d series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic radii (pm)	162	145	134	130	127	125	125	128	134	148
Elements of 5d series	La- Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic radii (pm)	169	144	134	130	128	126	127	130	136	150

From this table, it is evident that due to lanthanide contraction, the atomic and ionic radii of second and third transition series elements do not differ much though they are appreciably higher than those of first transition series elements. It is also observed that the atomic radii of the elements falling immediately after the lanthanide series are closer to those of their 4d-congeners and the effect slowly decreases along the series of 5d-elements as we move away from it.

(a) Densities of the elements of the three transition series:

The density and atomic volume are inversely proportional to each other. All the transition metals have low values for their atomic volumes and hence their densities are high. In a given transition series, the atomic volumes of the elements first decrease on proceeding from left to right and generally attain a minimum value for the elements of group VIII (i.e., Groups 8,9,10). They then start increasing further up to Group 12 elements. Accordingly, the density of the elements increases from left to right up to the elements of Group VIII (Groups 8,9,10) and then decreases up to Group 12.

Down the group, the densities of the elements increase regularly. But the striking feature that has been observed on moving from the first element to the last element in every group is that the densities of the elements belonging to second transition series are only slightly higher than those of the corresponding elements of 3d-series while the values for the elements from Hf ($Z=72$) to Hg ($Z=80$) (i.e., 5d-series) are almost double of those for the elements from Zr ($Z=40$) to Cd ($Z=48$), respectively (4d-series). This analogy does not apply to Y ($Z=39$) and La ($Z=57$). This can be explained as follows:

Because of lanthanide contraction, the atomic sizes of the elements of third transition series after La ($Z=57$) i.e. from Hf onwards become very small and as a result, the packing of atoms in their metallic crystals becomes much compact which results in high densities. Also, there is only a small difference in the atomic sizes of the elements of the two series, viz., 4d- and 5d-series but the atomic masses of the elements of 5d-series are almost double to the corresponding elements of 4d-series. This makes the densities of 5d-series elements almost double to those of the elements of 4d-series.

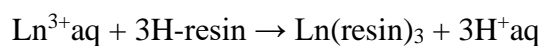
(b) Similarities among lanthanides:

There is very small change in the radii of lanthanides and hence their chemical properties are quite similar. This makes the separation of these elements using the usual physical and chemical methods difficult. Consequently, new methods like ion exchange technique, solvent extraction etc. have now been used for their separation which are based on slight difference in the properties like hydration, complex ion formation, etc.

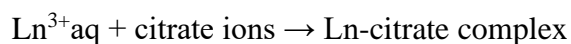
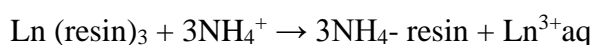
Separation of lanthanides by ion-exchange method

This is the most rapid and most effective method for the isolation of individual lanthanide elements from the mixture. An aqueous solution of the mixture of lanthanide ions (Ln^{3+}aq) is introduced into a column containing a synthetic cation exchange resin such as DOWAX-50

[abbreviated as HR (solid)]. The resin is the sulphonated polystyrene containing-SO₃H as the functional group. As the solution of mixture moves through the column, Ln³⁺aq ions replace H⁺ ions of the resin and get themselves fixed on it:



The H⁺aq ions are washed through the column. The Ln³⁺aq. ions are fixed at different positions on the column. Since, Lu³⁺aq. is largest (Lu³⁺ anhydrous is smallest and is hydrated to the maximum extent) and Ce³⁺aq. is the smallest, Lu³⁺aq. ion is attached to the column with minimum firmness remaining at the bottom and Ce³⁺aq. ion with maximum firmness remaining at the top of the resin column. In order to move these Ln³⁺aq. ions down the column and recover them, a solution of anionic ligand such as citrate or 2-hydroxy butyrate is passed slowly through the column (called elution). The anionic ligands form complexes with the lanthanides which possess lower positive charge than the initial Ln³⁺aq ions. These ions are thus displaced from the resin and moved to the surrounding solutions as eluant- Ln complexes. For example, if the citrate solution (a mixture of citric acid and ammonium citrate) is used as the eluant, during elution process, NH₄⁺ ions are attached to the resins replacing Ln³⁺aq. ions which form Ln-citrate complexes:



As the citrate solution (buffer) runs down the column, the metal ions get attached alternately with the resin and citrate ions (in solution) many times and travel gradually down the column and finally pass out of the bottom of the column as the citrate complex. The Ln³⁺aq cations with the largest size are, eluted first (heavier Ln³⁺aq ions) because they are held with minimum firmness and lie at the bottom of the column. The lighter Ln³⁺aq ions with smaller size are held

at the top of the column (with maximum firmness) and are eluted at last. The process is repeated several times by careful control of concentration of citrate buffer in actual practice.

CHEMISTRY OF THE ACTINIDE ELEMENTS

The group of fourteen elements from thorium (Th, $Z = 90$) to lawrencium (Lr, $Z=103$) are called actinides, actinoids or actinons. These are named so because these elements succeed the element actinium (Ac, $Z = 89$). These elements are also known as inner-transition elements as they lie between actinium and rutherfordium (Rf, $Z = 104$), i.e., the elements of fourth transition series. Thus, they constitute the second inner-transition series of which actinium is the prototype. In these elements 5f-subshell of the antepenultimate shell ($n=7$) is successively filled by the additional or differentiating electrons, one at a time in each step, which are embedded in the interior while 6d- and 7s-electons are exposed to the surroundings. In the outermost and penultimate shell of these elements, the number of electrons remains almost the same. That is why the actinide elements resemble one another very closely. The actinides lying beyond uranium, i.e., the elements with $Z = 93$ to 103 are called transuranium elements. The first and the last elements of 5f-series have been mentioned above with their names and symbols, i.e., Th and Lr. The remaining twelve elements are listed below:

protactinium (Pa, $Z = 91$), uranium (U, $Z = 92$), neptunium (Np, $Z = 93$), plutonium (Pu, $Z = 94$), americium (Am, $Z = 95$), curium (Cm, $Z = 96$), berkelium (Bk, $Z = 97$), californium (Cf, $Z= 98$), einsteinium (Es, $Z = 99$), fermium (Fm, $Z= 100$), mendelevium (Md, $Z = 101$) and nobelium (No, $Z= 102$).

ELECTRONIC CONFIGURATION

The electronic configuration of actinium ($Z = 89$) which is followed by fourteen actinides is $[\text{Rn}]5f^06d^17s^2$, the last electron entering the 6d-subshell. In the next element, Th, the first member of the actinide series, the additional electron must enter 5f-subshell and the filling of 5f-subshell must continue progressively till the last element, Lr. Thus, 6d-subshell in all the elements must remain singly filled thereby giving the expected valence shell configuration of $5f^{1-14}6d^17s^2$ for these elements. Since, the energies of 6d- and 5f- subshells are almost the same and the atomic spectra of the elements are very complex, it is difficult to identify the orbital in terms of quantum numbers as well as to write down the configuration. For chemical behaviour, the valence shell electronic configuration of the elements is of great importance and the competition between $5f^n6d^07s^2$ and $5f^{n-1}6d^17s^2$ is of interest. It has been observed that the electronic configuration of actinides does not follow the simple pattern as is observed for the lanthanides. For the first four actinide elements, viz., Th, Pa, U and Np, due to almost equal energies of 5f and 6d, the electrons may occupy the 5f or 6d subshells or sometimes both. From Pu ($Z=94$) onwards, 6d¹ electron gets shifted to 5f-subshell except for Cm ($Z=96$) and Lr ($Z=103$) in which 6d¹ electron does not shift to 5f due to stable $5f^7$ and $5f^{14}$ configurations. In view of the above considerations, the general valence shell electronic configuration of the actinide elements may be written as: $5f^{0-14}6d^{0-2}7s^2$. For individual elements the observed or actual valence shell configurations are listed below:

Element	Atomic No. (Z)	Electronic Configuration of outer orbital	
		M	M ³⁺
Actinium(Ac)	89	6d ¹ 7s ²	5f ⁰
Thorium (Th)	90	6d ² 7s ²	5f ¹
Protactinium (Pa)	91	5f ² 6d ¹ 7s ²	5f ²
Uranium (U)	92	5f ³ 6d ¹ 7s ²	5f ³
Neptunium (Np)	93	5f ⁴ 6d ¹ 7s ²	5f ⁴
Plutonium (Pu)	94	5f ⁶ 7s ²	5f ⁵
Americium (Am)	95	5f ⁷ 7s ²	5f ⁶
Curium (Cm)	96	5f ⁷ 6d ¹ 7s ²	5f ⁷
Berkelium (Bk)	97	5f ⁹ 7s ²	5f ⁸
Californium (Cf)	98	5f ¹⁰ 7s ²	5f ⁹
Einsteinium (Es)	99	5f ¹¹ 7s ²	5f ¹⁰
Fermium (Fm)	100	5f ¹² 7s ²	5f ¹¹
Mendelevium (Md)	101	5f ¹³ 7s ²	5f ¹²
Nobelium (No)	102	5f ¹⁴ 7s ²	5f ¹³
Lawrencium (Lr)	103	5f ¹⁴ 6d ¹ 7s ²	5f ¹⁴

From the above valence shell configurations of the actinide elements, it is clear that Th does not have any f-electron though this element belongs to 5f-series (i.e., actinides). For Pa, U, Np, Cm and Lr, both the expected and observed (actual) configurations are same. For the rest of the actinides, 6d-subshell does not contain any d-electron.

OXIDATION STATES

The important oxidation states exhibited by actinides are compiled below in the tabular form. Some of them are stable but most of these oxidation states are unstable. It may be seen from

these oxidation states that the +2 state is shown by Th and Am only in the few compounds like ThBr₂, ThI₂, ThS, etc. The +3 oxidation state is exhibited by all the elements and it becomes more and more stable as the atomic number increases. The +4 oxidation state is shown by the elements from Th to Bk, the +5 oxidation state by Th to Am, the +6 state by the elements from U to Am and the +7 state is exhibited by only two elements, viz., Np and Pu. Np in the +7 state acts as an oxidising agent. The principal cations given by actinide elements are M³⁺, M⁴⁺ and oxo-cations such as MO₂⁺ (oxidation state of M = + 5) and MO₂²⁺ (oxidation state of M = +6). The examples of oxo-cations are UO₂⁺, PuO₂⁺, UO₂²⁺ and PuO₂²⁺ which are stable in acid and aqueous solutions. Most of the M³⁺ ions are more or less stable in aqueous solution. Np³⁺ and Pu³⁺ ions in solution are oxidized to Np⁴⁺ and Pu⁴⁺ by air. The latter ions are further oxidized slowly to UO₂²⁺ and PuO₂²⁺ by air. Various oxidation states of the actinides are listed below:

Element	Oxidation states
Ac	+3
Th	+2, +3, +4
Pa	+3, +4, +5
U	+3, +4, +5, + 6
Np	+3, +4, +5, +6, +7
Pu	+3, +4, +5, +6, +7
Am	+2, +3, +4, +5, +6,
Cm	+3, +4
Bk	+3, +4
Cf	+3, +4
Es	+2, +3
Fm	+2, +3
Md	+2, +3
No	+2
Lr	+3

The lighter elements up to Am show variable oxidation states, the maximum being for Np, Pu and Am, but the heavier elements show oxidation state of +2 or +3.

MAGNETIC AND SPECTRAL PROPERTIES

It has already been mentioned that the paramagnetic nature of the substances is due to the presence of unpaired electrons. The actinide elements like lanthanides show paramagnetism in the elemental and ionic states. Tetravalent thorium (Th^{4+}) and hexavalent uranium (U^{6+}) ions are diamagnetic due to the absence of unpaired electrons. $\text{Th}^{4+} = \text{U}^{6+} = \text{Rn}$ ($Z= 86$) structure (diamagnetic, paired electrons). Since, actinides constitute second f-series, it is natural to expect similarities with lanthanides (the first f series) in their magnetic and spectroscopic properties. But, there are some differences between the lanthanides and actinides. Spin-orbit coupling is strong ($2000\text{-}4000\text{cm}^{-1}$) in the actinides as happens in the lanthanides but because of the greater exposure of the 5f-electrons, crystal field splitting is now of comparable magnitude and J is no longer such a good quantum number. It is also noted that 5f and 6d-subshells are sufficiently close in energy for the lighter actinides to make 6d levels accessible. As a result, each actinide compound has to be considered individually. This must allow the mixing of J levels obtained from Russel-Saunders coupling and population of thermally available excited levels. Accordingly, the expression $\mu = g \sqrt{J(J+1)}$ is less applicable than for the lanthanides and magnetic moment values obtained at room temperature are usually lower and are much more temperature dependent than those obtained for compounds of corresponding lanthanides.

The electronic spectra of actinide compounds arise from the following three types of electronic transitions:

(a) **f-f transitions:** These are Laporte (orbitally) forbidden but the selection rule is relaxed partially by the action of crystal field in distorting the symmetry of the metal ion. Because the actinides show greater field, hence the bands are more intense. These bands are narrow and

more complex, are observed in the visible and UV regions and produce the colours in aqueous solutions of simple actinide salts.

(b) **5f-6d transitions:** These are Laporte and spin allowed transitions and give rise to much more intense bands which are broader. They occur at lower energies and are normally confined to the UV region hence do not affect the colours of the ions.

(c) **Metal to ligand charge transfer:** These transitions are also fully allowed and produce broad, intense absorptions usually found in UV region, sometimes trailing in the visible region. They produce the intense colours which are characteristic of the actinide complexes.

The spectra of actinide ions are sensitive to the crystal field effects and may change from one compound to another. It is not possible to deduce the stereochemistry of actinide compounds due to complexity of the spectra. Most of the actinide cations and salts are coloured due mainly to f-f transitions. Those with f^0 , f^7 and f^{14} configurations are colourless. The colours of some of the compounds in different oxidation states are given below:

NpBr ₃ : green;	NpI ₃ : brown;	NpCl ₄ : red-brown;	NpF ₆ : brown
PuF ₃ : purple;	PuBr ₃ : green;	PuF ₄ : brown;	PuF ₆ : red brown
AmF ₃ : pink;	AmI ₃ : yellow;	AmF ₄ : dark tan.	

The coordination chemistry of actinides is more concerned with aqueous solutions. Because of the wider range of oxidation states available in actinides, their coordination chemistry is more varied. Most of the actinide halides form complex compounds with alkali metal halides. For example, ThCl₄ with KCl forms complexes such as K[ThCl₅] and K₂[ThCl₆], etc. ThCl₄ and ThBr₄ also form complexes with pyridine, e.g. ThCl₄.py Chelates are formed by the actinides with multidentate organic reagents such as oxine, EDTA, acetyl acetone, etc.

The actinides with small size and high charge have the greatest tendency to form complexes.

The degree of complex formation for the various ions decreases in the order: $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$. The complexing power of different anions with the above cations is in the order:

Monovalent anions : $F^- > NO_2^- > Cl^-$

Bivalent anions : $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

SIMILARITIES BETWEEN LANTHANIDES AND ACTINIDES

(i) In the atoms of the elements of both the series, three outermost shells are partially filled and remaining inner shells are completely filled but the additional or differentiating electron enters (n-2) f-subshell.

(ii) The elements of both series exhibit +3 oxidation state which is prominent and predominant state.

(iii) Like Lanthanide contraction found in the lanthanide elements, there occurs contraction in size in the actinide elements called **actinide contraction**. Both the contractions are due to poor shielding effect produced by f-electron with increasing nuclear charge.

(iv) The elements of both the series are quite reactive and are electropositive.

(v) The electronic absorption bands of the elements of both the series are sharp and appear like lines. These bands are produced due to f-f transitions within (n-2)f-subshell though such transitions are orbital forbidden.

(vi) Most of the lanthanide and actinide cations are paramagnetic.

(vii) The nitrates, perchlorates and sulphates of trivalent lanthanide and actinide elements are soluble while the hydroxides, fluorides and carbonates of these elements are insoluble.

(viii) The lanthanide and actinide elements show similarity in properties among their series though the lanthanides are closer among themselves in properties as compared to actinides.

DIFFERENCES BETWEEN LANTHANIDES AND ACTINIDES

Lanthanides	Actinides
1. From left to right along 4f series, the decrease of atomic size is not regular with increase in atomic number. But decrease of ionic radius is regular.	1. From left to right along 5f series, the decrease of atomic size and ionic radius is regular.
2. Along with +3 oxidation state, +2 and +4 oxidation state are also observed.	2. Along with +3 oxidation state, +4, +5, +6 and +7 oxidation state are also observed.
3. Lanthanide compounds are less basic.	3. Actinide compounds are more basic.
4. Ability to form complex compound is low.	4. Ability to form complex compound is high.
5. They do not form oxocation.	5. They form oxocation.
6. Except Pm, other lanthanides are non-radioactive.	6. All actinides are radioactive.

Questions:

1. What are the main differences in the magnetic and spectral behaviours among the elements of 4f and 5f series?
2. Explain briefly the principle of separation of lanthanides by ion exchange process.
3. What do you mean by Lanthanide contraction?
4. The third ionization energy for Eu and Yb are comparatively higher than other lanthanides---explain.
5. Pu^{3+} and the lighter actinides exhibit spectral features similar to those of transition metal ions but the spectra of Am^{3+} and the higher actinides are more lanthanide like---explain.
6. Explain why La^{3+} , Lu^{3+} are diamagnetic while Sm^{3+} has low paramagnetism.
7. Draw a comparison between lanthanides and actinides in terms of similarities and differences.
8. Lanthanides exhibit +3 oxidation state in general while actinides can show variable oxidation state---explain.
9. Eu^{3+} and Tb^{3+} are stable in addition to their common oxidation states-----explain.
10. State electronic absorption spectral features of lanthanides.
11. 'Usually colourful complexes are observed in actinides while most of the lanthanide complexes are colourless'----justify the statement with suitable example.
12. What is the main difference in magnetic behaviour among the elements of 4f, 5f and 3d series?
13. La^{3+} is diamagnetic but Eu^{3+} is not----explain.
14. Compare the patterns of electronic absorption bands of Lanthanides with those of transition metals with explanation.