magnetic moment due to the contribution of orbital motion of the electrons. The observed magnetic moment for $[Co(H_2O)_6]^{2+}$ has contribution from the spin as well as orbital angular momentum and thus the observed magnetic moment is higher than the calculated spin-only magnetic moment.

Answers to Terminal Questions

1. See the trends in properties.

2. Because of their noble nature gold and silver are used for making ornaments.

3. a) No metallic bond formation

   b) Ti(IV) has d^0 configuration

4.

	Ion	Electronic configuration	Number of unpaired electrons	Magnetic moment
a)	Fe^{2+}	$[Ar]3d^6 4s^0$	4	4.90 BM
b)	Mn^{7+}	$[Ar]3d^0 4s^0$	0	0 BM
c)	Cu^+	$[Ar]3d^{10}4s^0$	0	0 BM
d)	Ti^{3+}	$[Ar]3d^1 4s^0$	1	1.73 BM

5. a) Fe < Ru < Os

   b) Mo < Zr < Sr

   c) Sc < Y < La

6. (a) WO_3 (b) ReO_4^- (c) Cr^{3+} (d) Mn^{2+}

   (e) MoO_4^{2-} (f) Re_2O_7 (g) VO_4^{3-}

7. a) Reducing agent

   b) Oxidising agent

   c) Reducing agent

   d) Oxidising agent

8. Stability of high oxidation state as we go down a group.

9. a) $4Sc(s) + 3O_2(g) \longrightarrow 2Sc_2O_3(s)$

   b) $Ti(s) + O_2(g) \longrightarrow TiO_2(s)$

   c) $4(V)(s) + 5O_2(g) \longrightarrow 2V_2O_5(s)$

   d) $4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s)$

   e) $Mn(s) + O_2(g) \longrightarrow MnO_2(s)$

   f) $2Ni(s) + O_2(g) \longrightarrow 2NiO(s)$

   g) $2Cu(s) + O_2(g) \longrightarrow 2CuO(s)$

UNIT 13 INNER-TRANSITION ELEMENTS

Structure

13.1 INTRODUCTION

In the preceding unit, you studied the main features of the chemistry of the transition elements of the d-block. You learnt that in addition to the usual vertical relationship, the transition elements show a horizontal similarity in their physical and chemical properties. In this unit you will study the salient features of the chemistry of the transition elements of the f-block. Because of filling of electrons in the f-orbitals of an inner shell, these elements are also termed as inner-transition elements. The f-block elements comprise two series of elements — the lanthanide series and the actinide series. You will observe that in comparison to the elements of d-block transition series, the members of lanthanide series resemble one another much more closely. They have generally one common stable oxidation state and occur together in the same ores in nature. Because of the similarity in their chemical properties their separation from one another is very difficult. Therefore, special techniques of solvent extraction and ion exchange are employed for their separation. On the other hand, the chemistry of the actinides is quite complicated because they exhibit more than one oxidation state and their radioactivity creates problems in the study of their properties. However, the actinides do exhibit some similarities with one another and with their lanthanide congeners in a particular oxidation state. Therefore, these elements are discussed as a class in one unit. In this unit you will study the general features of the chemistry of lanthanide and actinide elements with emphasis on periodicity in their properties.

Objectives

After studying this unit you should be able to :

- distinguish between transition and inner-transition elements,

- define the terms lanthanides and actinides,

- compute the electronic configurations of lanthanide and actinide ions from the electronic configurations of free atoms,

- discuss the ways in which actinide elements resemble their lanthanide congeners,

- discuss the ways in which the actinides resemble more closely d-block transition elements,

- explain lanthanide and actinide contraction,

- describe general characteristics of lanthanide and actinide elements and bring out periodicity in their properties.

13.2 GENERAL CHARACTERISTICS

You know that the fourteen elements from cerium ($Z = 58$) to lutetium ($Z = 71$), which

follow lanthanum ($Z = 57$) in the periodic table, are called lanthanides, lanthanoids or lanthanons. Note that some authors include lanthanum also in lanthanides, but there is no general agreement on it. These elements are characterised by successive filling of $4f$ orbitals in their atoms. These elements along with lanthanum and yttrium were originally called as rare earth elements or simply rare earths. The word 'earth' was used because they occur as oxides, which in early usage meant earth, and the word rare was used because of the great difficulty in their separation from each other. Otherwise, these are not particularly rare in earth's crust. For example, lanthanum, cerium and neodymium are more abundant than lead. Even the scarcest of them, thulium, is as abundant as bismuth and more abundant than arsenic, cadmium, mercury or selenium, none of which is generally considered rare.

The fourteen elements from thorium ($Z = 90$) to lawrencium ($Z = 103$) following actinium in the periodic table are known as actinides, actinoids or actinons. They are analogous to the lanthanides and result from the filling of the $5f$ orbitals as the lanthanides result from the filling of $4f$ orbitals. Prior to 1940, only the naturally occurring actinides, i.e., thorium, protactinium and uranium were known. The remaining actinides have been produced artificially since then and are collectively known as transuranium elements.

13.2.1 Electronic Configuration and Position in Periodic Table

The outstanding feature of the lanthanide and actinide elements is the great similarity in physical and chemical properties which they display within each series. Reason for this unique behaviour of these elements lies in their electronic configuration.

You know that lanthanum, the element preceding the lanthanides in the periodic table, has the electronic configuration $[Xe]5d^1 6s^2$. Like lanthanum, the lanthanides also exhibit the stable oxidation state of +3. It is, therefore, expected that in these elements the successive electrons will be filled in the $4f$ orbitals, thereby the elements may have the electronic configuration from $[Xe]4f^1 5d^1 6s^2$ to $[Xe]4f^{14}5d^1 6s^2$. The actual ground state electronic configurations of lanthanide elements have been determined by atomic spectroscopy and are given in Table 13.1. You can see from the Table that there is an electron in $5d$ orbital only in Ce, Gd and Lu, in all other elements this electron is shifted to the $4f$ orbital. This type of shuttling of electrons can be understood in terms of the comparable energies of the $4f$ and $5d$ orbitals. Whether there is an electron in $5d$ orbital or not, is of little importance because the lanthanides mostly form ionic compounds in +3 oxidation state and the electronic configuration of M^{3+} ions varies in a regular manner from $[Xe]4f^1$ for Ce^{3+} to $[Xe]4f^{14}$ for Lu^{3+}, as shown in Table 13.1.

Table 13.1 : Some properties of lanthanum and the lanthanides

Z	Name	Symbol	Electronic configuration outside the [Xe] core Ln	Ln³⁺	Metallic radius pm	Ionic radius M^{3+} pm	E° (V) M^{3+}/M	Colour of Ln³⁺
57	Lanthanum	La	$5d^1 6s^2$	–	187	106	–2.52	Colourless
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$	183	103	–2.48	Colourless
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$	182	101	–2.46	Green
60	Neodymium	Nd	$4f^4 6s^2$	$4f^3$	181	100	–2.43	Lilac
61	Promethium	Pm	$4f^5 6s^2$	$4f^4$	–	98	–2.42	Yellow
62	Samarium	Sm	$4f^6 6s^2$	$4f^5$	179	96	–2.41	Yellow
63	Europium	Eu	$4f^7 6s^2$	$4f^6$	204	95	–2.41	Pale pink
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$	180	94	–2.40	Colourless
65	Terbium	Tb	$4f^9 6s^2$	$4f^8$	178	92	–2.39	Pale pink
66	Dysprosium	Dy	$4f^{10}6s^2$	$4f^9$	177	91	–2.35	Yellow
67	Holmium	Ho	$4f^{11}6s^2$	$4f^{10}$	176	89	–2.32	Yellow
68	Erbium	Er	$4f^{12}6s^2$	$4f^{11}$	175	88	–2.30	Rose pink
69	Thulium	Tm	$4f^{13}6s^2$	$4f^{12}$	174	87	–2.28	Pale green
70	Ytterbium	Yb	$4f^{14}6s^2$	$4f^{13}$	194	86	–2.27	Colourless
71	Lutecium	Lu	$4f^{14}5d^1 6s^2$	$4f^{14}$	174	85	–2.26	Colourless

The ground state electronic configuration of actinium, $[Rn]6d^1 7s^2$ is similar to that of lanthanum and indeed the two elements possess similar chemical properties. The electronic configurations of the elements that follow actinium are not known precisely; these are less certain than those of the lanthanide elements. The difference in energy between $5f$ and $6d$ orbitals in the beginning of the actinide series is less than that between the $4f$ and $5d$ orbitals

for the lanthanides. Therefore, both $5f$ and $6d$ orbitals are involved in accommodating successive electrons. Thus the filling of $5f$ orbitals in actinides (Table 13.2) is not quite so regular as the filling of the $4f$ orbitals in the case of the lanthanides. Later, however, the $5f$ orbitals become more stable, i.e., by the time plutonium and subsequent members of the series are reached, the $5f$ orbitals seem clearly to be of lower energy than the $6d$ orbitals, and so the electrons preferably fill the former.

Table 13.2 : Some properties of actinium and the actinides

Z	Name	Symbol	Electronic configuration outside the [Rn] core An	An^{3+}	Metallic radius pm	Ionic radius M^{3+} pm	E° (V) M^{3+}/M	Colour of An^{3+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$	–	112	–2.6	Colourless
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	179	–	–	–
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	163	104	–1.95	Colourless
92	Uraniun	U	$5f^3 6d^1 7s^2$	$5f^3$	156	103	–1.80	Red brown
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	155	101	–1.86	Purplish
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	155	100	–2.03	Blue violet
95	Americium	Am	$5f^7 7s^2$	$5f^6$	159	98	–2.38	Pink
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	173	97	–	Pale Yellow
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	174	96	–	–
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	170	95	–	–
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	186 ± 2	–	–	–
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	186 ± 2	–	–	–
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	–	–	–	–
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	–	–	–	–
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	–	–	–	–

SAQ 1

Explain briefly :

(a) What are inner-transition elements ?

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(b) What are lanthanides and actinides ? Why are they so called ?

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(c) Write the electronic configurations of the elements of atomic number 61 and 95.

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13.2.2 Atomic Radius

You have studied in Unit 2 that the atomic size decreases with increase in atomic number along any period in the long form of the periodic table due to increase in effective nuclear charge. However, the decrease in atomic radius is small when the difference in electronic configuration from one element to the next is that of an additional inner electron. This is because the additional inner electron screens the size-determining outer electrons from the nucleus much better than an additional outer electron. For example, decrease in the covalent radius from Sc to Zn, i.e., across ten elements of the $3d$ transition series, is 19 pm. This decrease is almost one-third of the decrease in the covalent radius of the seven elements of s and p blocks of the period 3.

The rate of decrease in atomic radius along the lanthanide series (Table 13.1) and also along the actinide series (Table 13.2) is even less than that in the transition series, since the difference in the electronic configurations of these elements is in the number of electrons in the ante-penultimate (last but two) shell of electrons. But the additive effect of decrease in atomic radius across the fourteen elements of lanthanide series is quite substantial. This decrease in atomic radius across the lanthanide series is known as lanthanide contraction. Similarly, there is an actinide contraction across the actinide series. As a result of lanthanide contraction, the normal increase in size from Sc→Y→La disappears after the lanthanides, and pairs of elements such as Zr and Hf, Nb and Ta, Mo and W, etc., possess nearly similar sizes (Table 13.3). The properties of these elements, therefore, are very similar. The similarities in properties within these pairs make their separation very difficult. Thus, due to lanthanide contraction, the elements of 5d and 4d transition series resemble each other much more closely than do the elements of 4d and 3d series.

Table 13.3: Atomic (covalent) radii of the elements preceding and following the lanthanides in pm

21		22	23	24	25	26	27	28	29	30
Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
144		132	122	118	117	117	116	115	117	125
39		40	41	42	43	44	45	46	47	48
Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
162		145	134	130	127	125	125	128	134	144
57	58–71	72	73	74	75	76	77	78	79	80
La	Ce–Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
169	165—156	144	134	130	128	126	127	130	134	147

SAQ 2

Explain the term lanthanide contraction and its consequences.

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13.2.3 Oxidation States

The sum of the first three ionisation energies of the lanthanides is comparatively low, so the elements are highly electropositive. They readily form M^{3+}. For the lanthanides, actinium and trans-americium (Cm to Lr) elements the tripositive oxidation state is the most stable in every case. It is believed that in forming tripositive lanthanide or actinide ions, the ns^2 ($n = 6$ or 7) electrons are lost along with the $(n-1)d^1$ electron. In the absence of $(n-1)d^1$ electron, one of the electrons present in the $(n-2)f$ orbitals is lost.

Besides the +3 state, some of the lanthanides and actinides show other oxidation states also. In these cases there is some evidence that ions with f^0 (e.g., La^{3+}, Ce^{4+}, Ac^{3+}, Th^{4+}, Pa^{5+}, U^{6+}) f^7 (e.g., Eu^{2+}, Gd^{3+}, Tb^{4+}, Cm^{3+}, Bk^{4+}), and f^{14} (e.g., Yb^{2+}, Lu^{3+}) configurations exhibit greater stability. However, Pr^{4+} ($4f^1$), Nd^{4+} ($4f^2$), Sm^{2+} ($4f^6$), Tm^{2+} ($4f^{13}$), etc. with non-f^0, non-f^7 and non-f^{14} electronic configurations also exist. This reminds us that there may be other factors also such as ionisation energies and sublimation energies of the metals and lattice energies, etc., which are responsible for the stability of these oxidation states. The known oxidation states of actinium and the actinides are given in Table 13.4 in which numbers in bold indicate the most stable oxidation state in aqueous solution. You can see from the Table that nearly all the actinides exhibit at least two stable oxidation states and oxidation states higher than +3 are easily accessible in the early actinides. For thorium, protactinium and uranium the highest accessible oxidation state is the most stable one also in aqueous solution. This may be because 5f orbitals extend further from the nucleus than the 4f orbitals and 5f electrons are more effectively shielded from the nuclear charge than are the 4f electrons of the corresponding lanthanides. Because the 5f electrons are less firmly held, they are all available for bonding in the early actinides. However, as the later actinides are approached, the build-up of nuclear charge causes contraction of the 5f orbitals so that the metal-ligand overlap decreases and the +3 state becomes predominant. Interestingly, the

+2 state which is achievable in case of mendelevium and nobelium, is more stable than Eu^{2+}.

Table 13.4: Oxidation states of actinium and the actinides. The more stable states are in bold type; unstable states are enclosed in parentheses.

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						(2)			(2)	(2)	2	2	2	–
3	(3)	(3)	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4	(4)					
		5	5	5	5	5								
			6	6	6	6								
				(7)	7									

SAQ 3

Which is the most common oxidation state of the lanthanides and how is it formed ? Give its configuration.

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13.2.4 Colour of Ions

Ions of lanthanides and actinides are coloured in the solid state as well as in aqueous solution, as is the case with the ions of transition metals. You have studied in the preceding unit that the colours of transition metal ions arise because of absorption of light due to $d - d$ electronic transitions. Because there are no electrons in the d–orbitals, the colours of lanthanide and actinide ions arise due to electronic transitions in the $4f$ and $5f$ orbitals. Colours of hydrated lanthanide and actinide ions are given in Table 13.1 and 13.2, respectively.

13.2.5 Electrode Potentials

The standard electrode potentials of lanthanides for the half- reaction,

$$Ln^{3+}(aq) + 3e \longrightarrow Ln\ (s)$$
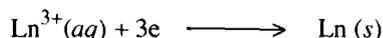
are given in Table 13.1. The electrode potentials are very low. Therefore, these elements are highly electropositive and reactive metals. The electrode potential increases from Ce to Lu, which is consistent with the slight decrease in the ionic radius due to lanthanide contraction. The electrode potentials of the actinide elements also are quite low (Table 13.2). Therefore, the actinides also are highly electropositive and reactive metals.

13.2.6 Complexation Behaviour

Ions of lanthanide and actinide elements have a strong tendency to form complexes with a variety of oxygen and nitrogen donor ligands. Probably, because of their comparatively higher charge to size ratio, the actinide ions have a greater tendency to form complexes than the lanthanides. Also, due to the existence of a large number of oxidation states, the complexation behaviour of actinides is more varied. The lanthanide and actinide ions form the most stable complexes with chelating ligands such as oxalic acid, citric acid, tartaric acid, nitric acid, ethylenediamine tetraacetic acid (EDTA) and β-diketones. In these complexes the metal ions have very high coordination numbers. For example, the coordination number of the metal ion in [Th(acac)4], [Ce(NO3)4·(OPPh3)2] and [Ce(NO3)6]$^{2-}$ is 8, 10, 12, respectively. In these complexes, the acetyl acetonate (acac) and the nitrate ligands are acting as bidentate ligands occupying two coordination sites around the metal ion. These metal ions form water soluble complexes with citric acid, tartaric acid and EDTA. The formation of water soluble complexes with these ligands facilitates separation of the metal ions by ion exchange chromatography which you will study in the next section.

13.2.7 Magnetic Properties

You have learnt in the preceding unit that paramagnetism is associated with the presence of unpaired electrons in a substance. The lanthanide and actinide ions, other than f^0 type (e.g.,

La^{3+}, Ce^{4+}, Ac^{3+}, Th^{4+}, Pa^{5+}, U^{6+}) and f^{14} type (e.g., Yb^{2+}, Lu^{3+}, Lr^{3+}), are all paramagnetic, because each of the seven f orbitals characterising inner-transition metal species (lanthanide and actinide) must contain a single electron before any pairing can take place (Hund's rule).

You have also studied that in case of transition elements, the contribution of orbital motion of electrons to paramagnetism is negligible and can be ignored. The magnetic moments of transition metal ions can be explained in terms of unpaired electrons present in d–orbitals. But the magnetic moments of only those lanthanide ions, which have f^0, f^7 and f^{14} configuration agree with the spin only value. In all other cases, the magnetic moment values are higher than those calculated on the basis of spin only formula. However, these can be explained by taking orbital contribution to magnetic moment also into account. In lanthanide ions, the $4f$ orbitals are comparatively better shielded from the surroundings by the overlying $5s$ and $5p$ orbitals than the d orbitals in transition metal ions. Therefore, the contribution of orbital motion to paramagnetism is not quenched.

Although actinides show a variation in magnetic properties similar to that of the lanthanides, the magnetic properties of the actinide ions are more complicated than those of the lanthanide ions. This in part arises from (i) the fact that the $5f$ electrons are nearer the surface of the atom and are easily influenced by the chemical environment, although not to the same extent as do the d electrons, and (ii) the less sharply defined distinctions between $5f$ and $6d$ electrons as compared with $4f$ and $5d$ electrons. From the above discussion it is clear that the magnetic moments of the f–block (inner transition) metal ions must be calculated taking into account both spin and orbital contributions.

13.2.8 Chemical Properties

The lanthanides are silvery-white, highly electropositive and reactive metals. They all react slowly with cold water and rapidly on heating to liberate hydrogen :

$$2M + 6H_2O \longrightarrow 2M(OH)_3 + 3H_2$$
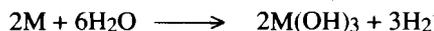
The hydroxides are ionic and basic. They are less basic than Ca $(OH)_2$ but more basic than amphoteric $Al(OH)_3$. The base strength decreases from $Ce(OH)_3$ to $Lu(OH)_3$ as the ionic radius decreases from Ce^{3+} to Lu^{3+}.

The lanthanide metals dissolve in dilute acids, even in the cold, to liberate hydrogen gas :

$$2Ln + 6HCl \longrightarrow 2LnCl_3 + 3H_2$$
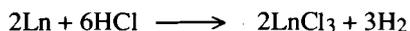
The metals tarnish readily in air forming an oxide coating. On heating in oxygen, they burn easily to give M_2O_3, except for cerium which forms CeO_2. The oxides are ionic and basic, the base strength decreases as the ionic radius decreases.

$$4Ln + 3O_2 \longrightarrow 2Ln_2O_3$$

When heated in halogens, the lanthanides burn producing LnX_3, which can also be made by heating the oxides with the appropriate ammonium halide :

$$2Ln + 3X_2 \longrightarrow 2LnX_3$$

$$Ln_2O_3 + 6NH_4X \longrightarrow 2LnX_3 + 6NH_3 + 3H_2O$$

Cerium with fluorine forms CeF_4 :

$$Ce + 2F_2 \longrightarrow CeF_4$$

The metals react exothermically with hydrogen, though heating to 600-700 K is often required to initiate the reactions. Their hydrides are non-stoichiometric compounds having ideal formulae, MH_2 and MH_3. The hydrides are remarkably stable to heat up to 1200 K. The hydrides react with water liberating hydrogen gas :

$$MH_3 + 3H_2O \longrightarrow M(OH)_3 + 3H_2$$
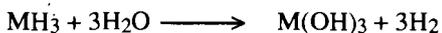
On heating, the lanthanides react with boron giving borides of the type MB_4 and MB_6, with carbon giving carbides M_2C_3 and MC_2 and with nitrogen giving nitrides MN. A wide variety of their oxosalts, like carbonates, sulphates, nitrates, phosphates, oxalate, etc., are known.

29

All the actinides are unstable with respect to radioactive disintegration, though the half-lives of the most abundant isotopes of thorium and uranium are so long that for many purposes their radioactivity can be neglected. Like lanthanides, actinides are also electropositive and reactive metals. They react with water, oxygen, hydrogen, halogens and acids. Their hydrides are non-stoichiometric having ideal formulae MH_2 and MH_3. The metals also react with most non-metals especially if heated.

SAQ 4

Write down the chemical equations for the reactions of lanthanide elements with   (i) water, (ii) acids, (iii) oxygen and (iv) halogens.

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13.3 OCCURRENCE, EXTRACTION AND USES

All the lanthanide and actinide elements are highly reactive metals, therefore, none of them occurs in the free state in nature. Moreover, all the actinide elements are radioactive, so most of them do not occur naturally and have been prepared artificially since 1940. Let us now discuss the occurrence, extraction and uses of these elements.

13.3.1 Occurrence

Apart from promethium which is unstable and is found in traces in uranium ores, all the lanthanides generally occur together. Although a large number of minerals are known to contain lanthanides, only three of them, viz., monazite, bastnaesite and xenotime are of commercial importance. Monazite and xenotime are a mixture of phosphates of thorium, lanthanum and lanthanides. Monazite is widely but sparsely distributed in many rocks, but because of its high density and inertness, it is concentrated by weathering into sands on beaches and river beds. Deposits of monazite occur in Southern India, South Africa and Brazil. Bastnaesite is a mixture of fluoride carbonates, $LnFCO_3$, of lanthanum and the lanthanides. Both monazite and bastnaesite are richer in the lighter lanthanides, i.e., the cerium earths, but with the difference that monazite also contains upto 30% ThO_2, which is absent in bastnaesite. On the other hand xenotime is a valuable source of the heavier rare earths.

Every known isotope of the actinide elements is radioactive and their half-lives are such that only ^{232}Th, ^{235}U, ^{238}U and possibly ^{244}Pu have survived during the very period of their existence. Only thorium and uranium are found in nature in amounts sufficient for practical extraction. Thorium constitutes 8.1×10^{-4}% of the earth's crust and it is almost as abundant as boron. As described earlier, monazite is the most important source of thorium. Uranium comprises 2.3×10^{-4}% the earth's crust and it is slightly more abundant than tin. Pitchblende or uraninite, U_3O_8, and carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$, are two important ores of uranium.

13.3.2 Extraction

As all the lanthanides occur together in nature, their extraction involves two main steps: (i) separation from one another and (ii) reduction of their compounds to metals. Since the lanthanides are all typically trivalent and are almost identical in size, their chemical properties are almost similar. Therefore, the separation of lanthanides from one another is a very difficult task, almost as difficult as the separation of isotopes. Only cerium and europium can be separated from the remaining lanthanides by employing conventional chemical methods because of stabilities of Ce^{4+} and Eu^{2+} in aqueous solution. Cerium can be separated from a mixture of lanthanides by oxidising Ce^{3+} to Ce^{4+} with permanganate or bromate or hypochlorite in an alkaline medium and subsequently precipitating it as CeO_2. Europium can be reduced to Eu^{2+} either by electrolytic reduction with a mercury cathode or by using zinc amalgam. It is then precipitated from the solution as $EuSO_4$.

Earlier the lanthanides used to be separated from each other by **selective precipitation** or by **fractional crystallisation**. With a limited amount of a precipitating agent, the substance which is least soluble is precipitated first. For example, if a base is added to a solution of lanthanide nitrates, the least soluble $Lu(OH)_3$ is precipitated first and the most soluble $La(OH)_3$ last. As only a partial separation is effected, the precipitate is redissolved and the process is repeated several times.

The solubility of double salts of lanthanides such as $2Ln(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ and $Ln_2(SO_4)_3 \cdot Na_2SO_4 \cdot xH_2O$ increases from La to Lu. Therefore, the lanthanides could be separated from each other oy **fractional crystallisation** of these salts. As these processes need to be repeated several times, these are very tedious and not very efficient. However, the individual elements can now be separated with much less difficulty on a large scale by employing more efficient techniques of **solvent extraction** and **ion exchange chromatography.**

The distribution coefficients of the salts of lanthanide elements between water and organic solvents are slightly different. Therefore, the individual elements are selectively extracted from aqueous solutions of their salts into an organic solvent. This technique of separation is known as solvent extraction. Tributyl phosphate is a very good solvent for this process. The solubility of lanthanides in +3 oxidation state in tributyl phosphate increases with atomic number. Separation is performed by using a continuous **counter-current process** in which the aqueous solution of lanthanide nitrates and the solvent are passed through a column continuously in opposite directions. This process is much less tedious than performing several crystallisations.

The process of **ion exchange chromatography** is the most important, rapid and effective method for the separation and purification of the lanthanons. In this process, a solution of lanthanide ions is run down a column of a synthetic ion exchange resin. Ion exchange resins are organic polymers consisting of functional groups such as $-COOH$, $-SO_3H$ or $-OH$. In these resins, hydrogen ions are mobile and can be exchanged with other cations. Thus, the lanthanide ions replace the H^+ ions and get bound to the resin :

$$Ln^{3+} + 3R - SO_3H \longrightarrow Ln(SO_3R)_3 + 3H^+$$

After the H^+ ions have passed through the column, a solution of a complexing agent such as citric acid, α–hydroxyisobutyric acid or EDTA at the appropriate pH is passed through the column to elute, i.e., to wash off the metal ions in a selective manner :

$$Ln(O_3SR)_3 + (NH_4)_3EDTAH \longrightarrow Ln(EDTAH) + 3NH_4O_3SR$$

As the EDTA solution flows down the column, the lanthanide ions come off the resin and form a complex with EDTA and then go back on the resin a little lower down the column. This process is repeated many times as the metal ions gradually travel down the column. The smaller lanthanide ions like Lu^{3+} form stronger complexes with EDTA than the larger ions like La^{3+}. Thus, the smaller and heavier ions spend more time in solution and less time on the column. Therefore, the heavier ions are eluted from the column first and the lighter ones the last. Using suitable conditions, all the individual elements can be separated. The eluates are then treated with an oxalate solution to precipitate lanthanides as oxalates which are then ignited to get the oxides :

$$2Ln(EDTAH) + 3(NH_4)_2C_2O_4 \longrightarrow Ln_2(C_2O_4)_3 + 2(NH_4)_3EDTAH$$

$$Ln_2(C_2O_4)_3 \longrightarrow Ln_2O_3 + 3CO + 3CO_2$$

Samarium, europium and ytterbium are prepared by reduction of the oxides with La at high temperatures :

$$Ln_2O_3 + 2La \longrightarrow La_2O_3 + 2Ln, \ Ln = Sm \text{ and } Eu$$

Other lanthanides are obtained by the reaction of $LnCl_3$ or LnF_3 with Ca metal at 1300 K. $LnCl_3$ or LnF_3 are prepared by heating Ln_2O_3 with appropriate ammonium halide :

$$Ln_2O_3 + 6NH_4X \longrightarrow LnX_3 - 6NH_3 + 3H_2O$$

$$2LnX_3 + 3Ca \longrightarrow 2Ln + 3CaX_2$$
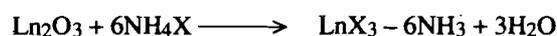
You know that actinium and all the actinides are radioactive. Of these only thorium and uranium are extracted from ores, all others are prepared artificially by nuclear reactions. The chief ores of thorium and uranium are monazite and pitchblende, respectively. For extraction

of thorium, monazite is dissolved in concentrated sulphuric acid. By suitably adjusting the pH of this solution, a precipitate of ThO_2 is obtained. The impure ThO_2 is purified by dissolving it in hydrochloric acid and then extracting $ThCl_4$ by tributyl phosphate. From this solution ThO_2 is reprecipitated by adjusting the pH. Purified ThO_2 is converted into anhydrous ThF_4 or $ThCl_4$ by the action of HF or CCl_4 at 900K. Thorium metal is then prepared by reduction of ThF_4 or $ThCl_4$ with calcium :

$$ThX_4 + 2Ca \longrightarrow Th + 2CaX_2$$

Uranium is chiefly extracted from pitchblende. The concentrated ore (pitchblende, U_3O_8) is washed and then fused with sodium carbonate and sodium nitrate. The fused mass is treated with sulphuric acid, which extracts uranyl sulphate, UO_2SO_4. Addition of sodium carbonate solution in excess to the above solution, removes all the heavy metals as carbonates. Uranium goes in solution as sodium uranyl carbonate $Na_4[UO_2(CO_3)_3]$. Addition of dilute H_2SO_4 to the uranyl carbonate solution precipitates uranium as sodium diuranate, $Na_2U_2O_7$, which on treatment with concentrated solution of $(NH_4)_2CO_3$ passes into solution as ammonium uranyl carbonate, $(NH_4)_4[UO_2(CO_3)_3]$. Concentration of this solution gives pure U_3O_8. Reduction of U_3O_8 with aluminium powder produces uranium metal. All these steps involved in extraction of uranium from pitchblende are summarised in a flow sheet.
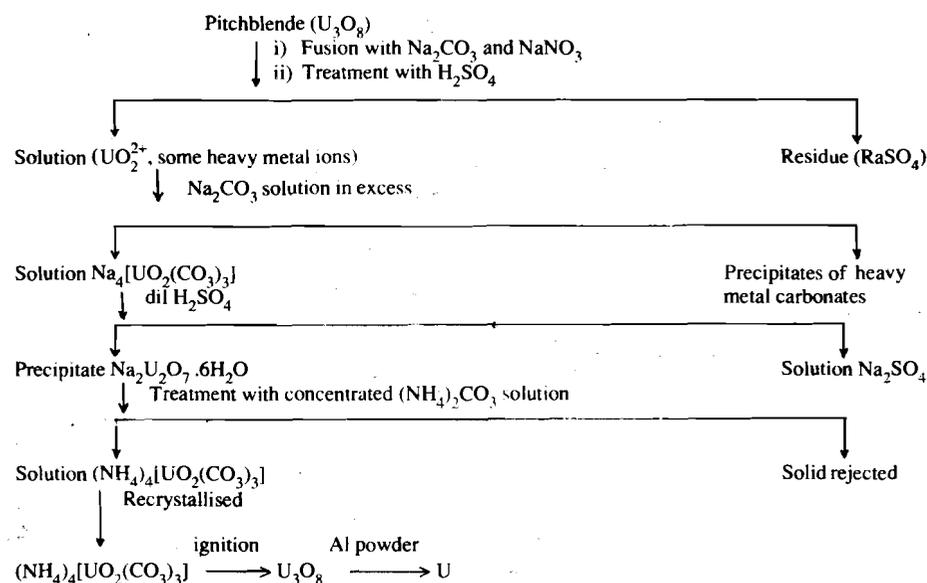
Flow sheet for extraction of uranium from pitchblende

13.3.3 Uses

Lanthanides and many of their complexes have received wide industrial applications. For example, europium derivatives are used as phosphors in TV screen; samarium-cobalt alloys are used for making magnets, Pr_2O_3 and Nd_2O_3 are used for making welder's goggles, yttrium-aluminium garnets (YAG) are used both in electronic equipment and as synthetic gems. Various mixed oxides are used as catalysts in cracking of petroleum. Cerium in the +4 oxidation state is used as an oxidising agent in quantitative analysis. Thorium nitrate has been used for more than a century in gas mantles. Till 1940, the only industrial application of uranium was as a colouring material in the manufacture of yellow glass. At present, the principal use of thorium and uranium is as a nuclear fuel.

SAQ 5

Why is the separation of the lanthanides so difficult ? List three important methods used for the separation of lanthanide metals.

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13.4 SUMMARY

In this unit, you have studied electronic structures, oxidation states, magnetic properties, electrode potentials, chemical properties, occurrence, extraction and uses of lanthanides and actinides which can be summarised as following :

- The lanthanide and actinide elements are characterised by filling of $4f$ and $5f$ subshells, respectively.

- For the lanthanides, actinium and transamericium elements, the tripositive oxidation state is the most stable in every case. However, the oxidation states higher than +3 are quite common for the early actinide elements.

- The lanthanides exhibit greater similarities in their properties in their most prominent oxidation state, +3. Cerium and europium are the only lanthanides to be stable as Ce^{4+} and Eu^{2+} in aqueous solution.

- All the lanthanide and actinide ions which have unpaired electrons are paramagnetic. Paramagnetism of lanthanide and actinide ions depends on both spin and angular momentum of the unpaired electrons.

- All the lanthanides and actinides are highly electropositive and reactive metals. They react with oxygen, halogens, hydrogen, water and acids. Their hydrides are non-stoichiometric compounds.

- Cerium is the most abundant of all the lanthanides. Its main ores are monazite and bästnaesite.

- Since the lanthanides are all typically trivalent and are almost identical in size, their chemical properties are almost similar. As all the lanthanides occur together in nature, their separation is extremely difficult. Separation of lanthanides is effected by using the techniques of solvent extraction and ion-exchange chromatography. The metals are prepared by reduction of their oxides, chlorides or fluorides with La or Ca.

- Thorium and uranium are extracted from monazite and pitchblende, respectively. All other actinides are now prepared artificially by nuclear reactions.

13.5 TERMINAL QUESTIONS

1.   What are f–block elements ?

2.   What are rare earth elements ? Why are they so called ?

3.   Discuss the ways in which the actinide elements resemble their lanthanide congeners.

4.   Discuss the ways in which the early actinide elements more closely resemble normal transition elements.

5.   Discuss the position of lanthanide and actinide elements in the periodic table.

6.   Why most of the lanthanide and actinide compounds are paramagnetic ?

7.   Why the range of oxidation states is much more restricted in the lanthanide series as compared to the early actinides ?

13.6 ANSWERS

Answers to Self Assessment Questions

1.   (a)   Two series of elements from cerium (atomic number 58) to lutecium (atomic number 71) and thorium (atomic number 90) to lawrencium (atomic number 103) are known as inner-transition elements. The term transition is used because they exhibit transition behaviour by exhibiting variable oxidation states, forming coloured ions and exhibiting paramagnetism. The prefix inner is used because in the building up process of their atoms the differentiating electron enters the f orbitals of an inner shell.

(b)   The 14 elements from cerium (atomic number 58) to lutecium (atomic number 71) which follow lanthanium (atomic number 57) in the periodic table are called

lant!anides. Similarly, 14 elements from thorium (atomic number 90) to lawrencium (atomic number 103) which follow actinium (atomic number 89) in the periodic table are called actinides.

(c) The electronic configuration of the elements of atomic number 61 and 95 is $[Xe]4f^5 6s^2$ and $[Rn]5f^7 7s^2$, respectively.

2. The gradual decrease in atomic size of the lanthanide elements starting from cerium to lutecium is known as lanthanide contraction. Because of lanthanide contraction, the elements from hafnium to mercury that follow the lanthanides have unusually small sizes.

3. The most common oxidation state of lanthanides is +3. This oxidation state of the lanthanide ions arises due to the loss of two $6s$ electrons and the lone $5d$ electron, if present, from the atom of the elements. If no electron is present in the $5d$ orbital, then one of the electrons from the $4f$ shell is lost. The lanthanide ions in this oxidation state have the general configuration $[Xe]4f^{1-14}$.

4. i) $2Ln + 6H_2O \longrightarrow 2Ln(OH)_3 + 3H_2$

   ii) $2Ln + 6H^+ \longrightarrow 2Ln^{3+} + 3H_2$

   iii) $4Ln + 3O_2 \longrightarrow 2Ln_2O_3$

   $Ce + O_2 \longrightarrow CeO_2$

   iv) $2Ln + 3X_2 \longrightarrow 2LnX_3$

   $Ce + 2F_2 \longrightarrow CeF_4$

5. The most stable oxidation state of the lanthanide elements is +3. The ionic radius of Ln^{3+} ions is quite comparable and varies very little from one element to another. Therefore, the chemical properties of the lanthanides are almost similar due to which the separation of lathanides is very difficult — almost as difficult as the separation of isotopes. The three most important methods which can be used for the separation of lanthanides are fractional crystallisation, solvent extraction and ion exchange chromatography.

Answers to Terminal Questions

1. Those elements, in the building up process of whose atoms the differentiating electron enters the *f* orbitals of an inner shell, are called *f*-block elements. There are two series of *f*-block elements containing 14 elements each. The lanthanide series contains elements from cerium to lutecium and the actinide series contains elements from thorium to lawrencium.

2. A group of elements, which includes the lanthanides, lanthanum and yttrium, is known as rare earth elements or simply rare earths. The word earth is used because these elements occur as oxides which in early usage meant earth, and the word rare was used because of great difficulty in their separation from each other.

3. Actinide elements resemble their lanthanide congeners in the following ways :
   • They have the similar electronic configurations,
   • They exhibit a common oxidation state of +3,
   • They form complexes,
   • Most of them form coloured ions and exhibit paramagnetism.

4. The early actinide elements exhibit a large number of oxidation states. In this respect they resemble normal transition elements.

5. There is no separate place for lanthanide and actinide elements in the periodic table. Therefore, the lanthanides are placed along with lanthanum and actinides along with actinium in the periodic table. Customarily, they are listed separately in two series at the bottom of the periodic table.

6. Most compounds of lanthanides and actinides are paramagnetic because they contain lanthanide and actinide ions which possess unpaired electrons. Presence of unpaired electrons gives rise to paramagnetism in the compound.

7. The range of oxidation states is much more restricted in the members of lanthanide series as compared to those of the actinide series. This is a result of stabilising effects

exerted on 4f orbitals by increasing ionic charge. By the time an ionic charge of +3 is developed on a lanthanide ion, the 4f orbitals are so stabilised that they become part of the inner core of the electrons. It becomes increasingly difficult to remove further electrons to give rise to higher oxidation states. On the other hand, in the beginning of the actinide series, the difference in energy of the 5f and 6d orbitals is much less. Therefore, 5f electrons along with 6d and 7s electrons participate in bonding, resulting in a wider range of oxidation states. However, later the 5f orbitals also become more stable and show reluctance to involve themselves in bonding.

UNIT 14   COORDINATION COMPOUNDS

Structure

14.1   INTRODUCTION

In Unit 12 of this block you have learnt about transition metals and their tendency to form coordination compounds or complexes. In this unit we shall study such complexes in more detail in view of their interesting chemistry and growing importance in chemical and biochemical processes. The complexes show a wide variety of physical and chemical properties which are quite different from normal salts. These differences arise due to the differences in their structures. In view of a special mode of bonding called 'coordination' being involved in their formation, they are also termed as coordination compounds. In this unit we shall briefly look at some of the basic definitions related to coordination compounds, familiarise you with different types of isomerism possible in them as well as the basic rules for naming these compounds. We shall then explain the formation of complexes in terms of different prevalent theories. However, we shall not deal with some other aspects, such as their thermodynamic and kinetic stability and reaction mechanism. These cannot be dealt with satisfactorily in such a short course. Finally, we shall consider a few applications of complexes in different fields.

Objectives

After studying this unit you should be able to:
- define the terms coordination compounds, coordination number, ligand and oxidation state,
- describe IUPAC rules for naming coordination compounds,
- name the coordination compounds according to IUPAC rules,
- write the formulae of coordination compounds if the systematic names are provided,
- describe the types of isomerism in coordination compounds,
- compare and contrast the different theories of bonding as applied to coordination compounds,
- explain geometries, magnetic and spectral properties of coordination compounds in terms of different bonding theories, and
- discuss the applications of coordination compounds in analytical chemistry, living systems and industry.