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B.Sc. 2nd Year

Inorganic Chemistry Paper-I UNIT-III Chapter- 4 PART-I

THE CHEMISTRY OF LANTHANIDES



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PART-I

THE CHEMISTRY OF LANTHANIDES

What are f-block elements? The elements which have partly filled forbitals constitute f-bock elements, after lanthanum in third transition series and in fourth transition series, after actinium. f-block divided into two series lanthanide(Z=57-71) and actinide series (Z=89-103).

Introduction

But it is situated just below the main body of the periodic table. Each series contains fifteen elements with lanthanum and actinium but La(Z=57) and Ac(Z=89) are actually d-block or transition element. Inner transition elements are highly electropositive in nature and show a common oxidation state of +3 and generally, similar in their physical and chemical properties. The only lanthanide that does not occur naturally is promethium, which is made artificially by nuclear reaction. It provides 20% total supply of lanthanides and also very small amount of genotype mineral. Lanthanides (also called lanthanones) are called first inner transition series and come immediately after lanthanum i.e. Ce-Lu (Z=58-71). They are commonly called the rare earth elements the word Earth was used because it occurred as oxides and word rare used because their occurrence was believed to very scarce.Now many more elements occur even morte rarely than the lanthanides. They are characterized by the filling up of the 4f energy levels which are not usually involved in bonding.

Table-1Electronic configuration, Oxidation states and Atomic andIonic Radii

Elements	Sym bol	Atomic No.	Electronic configuration of Atom and Ion(M ⁺³)	Oxidat ion State	Sum of First three ionization energy(KJmo l ⁻¹)	Atomic Radius(^Å) (ionic radius M ³⁺) (^Å)
Lanthanum	La	57	2.8.18.18.8(1).2 [Xe]4f ⁰ 5d ¹ 6s ² [Xe] 4f ⁰ 5d ⁰ 6s ⁰	+3	3493	1.68 (1.06)
Cerium	Се	58	2.8.18.18.8(2).8.2 [Xe]4f ² 5d ⁰ 6s ² [Xe]4f ¹ 5d ⁰ 6s ⁰	+3 +4	3512	1.62 (1.03)
Praseodymium	Pr	59	2.8.18.18(3).8.2 [Xe]4f ³ 5d ⁰ 6s ² [Xe]4f ² 5d ⁰ 6s ⁰	+3 (+4)	3623	1.83 (1.01)
Neodymium	Nd	60	2.8.18.18(4).8.2 [Xe]4f ⁴ 5d ⁰ 6s ² [Xe]4f ³ 5d ⁰ 6s ⁰	(+2) +3 +4	3705	1.82 (0.99)
Promethium	Pm	61	2.8.18.18(5).8.2 [Xe]4f ⁵ 5d ⁰ 6s ² [Xe]4f ⁴ 5d ⁰ 6s ⁰	(+2) +3	-	- (0.98)
Samarium	Sm	62	2.8.18.18(6).8.2 [Xe]4f ⁶ 5d ⁰ 6s ² [Xe]4f ⁵ 5d ⁰ 6s ⁰	(+2) +3	3898	1.80 (0.96)
Europium	Eu	63	2.8.18.18(7).8.2 [Xe]4f ⁷ 5d ⁰ 6s ² [Xe]4f ⁶ 5d ⁰ 6s ⁰	(+2) +3	4033	2.05 (0.95)

Gadolinium	Gd	64	2.8.18.18(7).8(1).2	+3	3744	1.80
			$[Xe]4f^{7}5d^{1}6s^{2}$			(0.94)
			[Xe]4f ⁷ 5d ⁰ 6s ⁰			
Terbium	Tb	65	2.8.18.18(9).8.2	+3 +4	3792	1.78
			$[Xe]4f^95d^06s^2$			(0.92)
			$[Xe]4f^{8}5d^{0}6s^{0}$			
Dysprosium	Dy	66	2.8.18.18(10).8.2	+3 +4	3898	1.77
	-		$[Xe]4f^{10}5d^{0}6s^{2}$			(0.91)
			[Xe]4f ⁹ 5d ⁰ 6s ⁰			
Holmium	Но	67	2.8.18.18(11).8.2	+3	3937	1.77
			$[Xe]4f^{11}5d^{0}6s^{2}$			(089)
			[Xe]4f ¹⁰ 5d ⁰ 6s ⁰			
Erbium	Er	68	2.8.18.18(12).8.2	+3	3908	1.76
			$[Xe]4f^{12}5d^{0}s^{2}$			(0.88)
			[Xe]4f ¹¹ 5d ⁰ 6s ⁰			
Thulium	Tm	69	2.8.18.18(13).8.2	(+2) +3	4038	1.75
			$[Xe]4f^{13}5d^{0}6s^{2}$			(0.87)
			[Xe]4f ¹² 5d ⁰ 6s ⁰			
Ytterbium	Yb	70	2.8.18.18(14).8.2	(+2) +3	4197	1.94
			$[Xe]4f^{14}5d^{0}6s^{2}$			(0.86)
			[Xe]4f ¹³ 5d ⁰ 6s ⁰			
Lutetium	Lu	71	2.8.18.18(14).8(1).	+3	3898	1.73
			2			(0.85)
			$[Xe]4f^{14}5d^{1}6s^{2}$			
			[Xe]4f ¹⁴ 5d ⁰ 6s ⁰			

Electronic Configuration-Electron in the lutetium atom enters in the 5d shell ([Xe] $4f^{14}5d^{1}6s^{2}$). Only lanthanum, gadolinium and lutetium have single 5d electrons. This is due to f,⁰ f,⁷ f,¹⁴ configuration i.e. empty, half field and completely field f-subshell. The other lanthanides generally may do not have electrons on their 5d orbitals.

Similarities in between lanthanide and Actinides

1. In both series, there is regular filling of f-subshell by electron one at each step.

- 2. Both are electropositive and have high chemical reactivity.
- 3. Both show common oxidation state of +3.
- 4. Both of them show f-f transition and they produce coloured compound.
- 5. Both show paramagnetic characteristics due to unpaired electrons.

6. In both series, atomic and ionic radii gradually decreases and show contraction.

General properties: Physical properties

Because of their close atomic size, they have following similar properties.

- 1. The metals are silvery white in colour.
- 2. They generally have high melting and boiling points and are very hard.
- 3. They are good conductors of heat and electricity.
- 4. Many of the lanthanide ions form colored ions.
- 5. The lanthanides exhibit a principal oxidation state or stable common oxidation state of +3 in which the M⁺³ ions are produced.

6. They exhibit parmagnetism because of the presence of unpaired electrons.

Abundance: The abundance of lanthanides is given the following table. **Table -Abundance of the elements and number of isotopes**

Atomic No.	Element	Abundance(ppm)in earth crust	Relative abundance	Naturally occurring isotopes
58	Се	66	26	4
59	Pr	9.1	37	1
60	Nd	40	27	7
61	Pm	0	-	0
62	Sm	7	40	7
63	Eu	2.1	49	2
64	Gd	6.1	41	7
65	Tb	1.2	56	1
66	Dy	4.5	42	7
67	Но	1.3	55	1
68	Er	3.5	43	6
69	Tm	0.5	61	1
70	Yb	3.1	44	7
71	Lu	0.8	59	2

Ionic Radii

The most stable ions of M³⁺ oxidation state is given **table-1**. The ionic size gradually decreases from moving left to right in lanthanide series (i.e.La³⁺

to Lu³⁺). The ionic radius shows a steady decrease from 1.06 A⁰ to 0.85 A⁰. This steady decrease in ionic radius along the series amounting total reduction to 0.21 A⁰, is called Lanthanide contraction.

Penetration by 4f, 5s, 5p electron: lanthanide contraction In these elements, the outer 6s electrons will spend most of their time outside a spherical charge cloud containing the 67 electrons of the xenon core and 4f sub-shell with the nucleus. This intervening charge cloud protects the 6s electrons from the full force of the +69 e nuclear charge. One way of looking at this is to say that the like-charged cloud repels them. The electron cloud shields them so that they experience an effective nuclear charge which is much less than the raw value of +69 e. For example, if we imagine a situation in which one 6s electron is as usual well outside the core while the other is unusually inside it then a charge cloud of 68 electrons will shield the outermost electron.

This suggests that, for most of the time, the 4f electrons penetrate more deeply into the core than the 5s and 5p. There are therefore fewer electrons to shield them from the nuclear charge, so they should be more tightly bound. Further as we move through lanthanide series, 4f electrons are being added one at each step. The shielding effect is also little of f-orbital, even smaller than d-orbital electrons. Meanwhile, the nuclear charge increases by one at each step. This in ward pull of 4f electrons increases. Consequently, a decrease in the size of the entire 4fⁿ subshell. The some of the successive reduction gives the Lanthanide contraction.

Unlike the 4f electrons, the 5s and 5p electrons sometimes penetrate deeply into the core and spend an appreciable time very close to the nucleus.We have seen that, during their motion, the 5s and 5p electrons spend a significant part of their time very close to the nucleus where they experience very large values of Z at very small distances r. This makes the energies of the 5s and 5p electrons more negative than the 4f and of the three types of electron, 4f much the most easily removed from the atom. Because the 4f electrons are short on penetration, they can make a contribution to the bonding in lanthanide compounds in spite of their position inside the xenon core.

Colour Of Lanthanide ions

Lanthanides are silvery white in appearance. Their ion in +3 oxidation states are coloured in solid state as well as n aqueous solution both. The colour is mainly arise due to presence of unpaired electrons and f-f transition in f-orbitals. Thus, these unpaired electrons absorb light in visible region of the spectrum, result the electronic transition within the 4f orbital. The various colors are shown in the following table for the different trivalent ions of Lanthanides.

lons	No. Of electrons	Colour
(+3)	in 4f subshell	
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
Lu ³⁺	4f ¹⁴	Colourless
Yb ³⁺	4f ¹³	Colourless
Tm ³⁺	4f ¹²	Green
Er ³⁺	4f ¹¹	Lilac
Ho ³⁺	4f ¹⁰	Pink
Dy ³⁺	4f ⁹	Yellow
Tb ³⁺	4f ⁸	Pale pink
Ce ⁴⁺	4f ⁰	Orange-red
Sm ²⁺	4f ⁶	Yellow
Eu ²⁺	4f ⁷	Pale greenish yellow
Yb ²⁺	4f ¹⁴	Colourless

Table -3 The Colours of Some Aqueous ios of Lanthanides

Electronic absorption spectra

The absorption band observed in visible region of spectrum also arise due to unpaired electron in the 4f- orbital, which absorbs light energy and show a bands or Sharpe lines in visible or near infrared region. The bands are slightly sharp unlike bands of d-d type transition. Since electron which absorb radiation are present in f-orbital, deeply inside the atom, thus shielded more effectively from ligand nature and their numbers which forms the complexes with metal ions.

Magnetic properties

The 4f electrons are responsible for the strong magnetism exhibited by the metals and compounds of the lanthanides. In the incomplete 4f subshell the magnetic effects of the different electrons do not cancel out each other as they do in a completed subshell, and this factor gives rise to the interesting magnetic behavior of these elements. At higher temperatures, all the lanthanides except lutetium are paramagnetic and this paramagnetism frequently shows a strong anisotropy. As the temperature is lowered, many of the metals exhibit a point below which they become anti ferromagnetism (i.e., magnetic moment of the ions are aligned but some are opposed to others) and as the temperatures are lowered still further, many of them go through a series of spin rearrangements, which may or may not be in conformity with the consistent crystal lattice. Finally, at still lower temperatures, a number of these elements become ferromagnetic (i.e., strongly magnetic, like iron). Some of the metals have saturation moments (magnetism observed when all the magnetic moments of the ions are aligned) greater than iron, cobalt, or nickel. They also show a strong anisotropy in them. The magnetic moment of f-block elements are calculated by following expression.

$\mu_J = g\sqrt{J(J+1)}$ BM, 1 BM = $\frac{eh}{2\pi mc}$ = 9.27 x 10⁻²¹ erg/gauss/particles g = 1+ $\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$

BM = Bohr Magneton, g = gyromagnetic ratio, J = total angular momentum of atom i.e. (L-S) or (L+S), ($f^0 \rightarrow f^7$ or $f^8 \rightarrow f^{14}$) L= resultant orbital quantum number, S=resultant spin quantum number.

Metallic properties

The hardness, melting and boiling points of the elements all increase from Ce to Lu due to attraction between the atoms increase as the size decreases. This makes them good conductors of electricity and heat.

Coordination Complexes

Ln³⁺ forms complexes of high coordination numbers. The coordination numbers for $[Ln(OH_2)_n]^{3+}$ in aqueous solution are up to 9 for the early lanthanoids and 8 for the later smaller members. The Ln³⁺ ions readily form complexes with F- and O-donor ligands eg H₂O, EDTA, β-diketones, citric acid, oxalic acid ligands. Partially fluorinated β-diketone ligand CF₃COCHCOCF₃ produces complexes with Ln³⁺ that are volatile and soluble in organic Solvents {because of their volatility, they are used as precursors for the synthesis of lanthanoid- containing superconductors by vapor deposition} Charged ligands have highest affinity for the smallest Ln³⁺ ion.

Coordination	Complex	Shape	
number			
4	[Lu(2,6-dimethylphenyl)4]	Tetrahedral	
6	$[Ce^{IV}CI_6]^{2}$	Octahedral	
6	[Er (NCS) ₆]	Octahedral	
7	[Y(acetylacetone) ₃ H ₂ 0]	Mono-capped trigonal	
		prism	
8	[La(acetylacetone) ₃ (H ₂ 0) ₂]	Square antiprism	
8	[Ce ^{IV} (acetylacetone) ₄]	Square antiprism	
8	[Eu(acetylacetone)₃(phenanthroline)]	Square antiprism	
8	[Ho(tropolonate) ₄]	Dodecahedral	
9	[Nd (H ₂ O) ₉] ³⁺	Tri-capped trigonal	
		prism	
9	[Sm (NH₃)9] ³⁺	Tri-capped trigonal	
		prism	
10	[Ce ^{IV} (CO ₃ -O, O)₅] ⁶⁻		
10	[Ce ^{IV} (NO ₃) ₄ (Ph ₃ PO) ₂]	(each nitrate ion is	
		bidentate)	
11	[La (OH ₂) ₅ (NO ₃ -O, O) ₃] ²⁻		
12	[Ce ^{IV} (NO ₃) ₆] ²	Icosahedral(each	
		nitrate ion is	
		bidentate)	
12	[La (NO) ³⁻		
	[La (OH ₂) ₂ (NO ₃ -O, O) ₅] ²⁻		

Table -4 Examples of Metal complexes

Chemical Properties of Lanthanides

In chemical reactivity, they resemble calcium.

1. They **readily tarnish** in air and burn to give oxides (all give trioxides except Ce which forms **CeO**₂)

2. They also combine with the following non-metals —N, S, halogens, H.

3. The hydrides are **non-stoichiometric** but have a composition of MH_3 . These hydrides liberate hydrogen from water.

4. The lanthanides also liberate hydrogen from water as does their hydrides and a vigorous evolution of same gas from dilute non-oxidizing acids.

$2Ln_{(s)} + 6H_2O_{(I)} = 2Ln(OH)_{3(aq)} + 3H_{2(g)}$

5. Lanthanide compounds are generally predominantly ionic and usually contain lanthanide metal in its **+3 0xidation states**.