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Chemistry of f-Block Elements

Class-T.Y.B.Sc.

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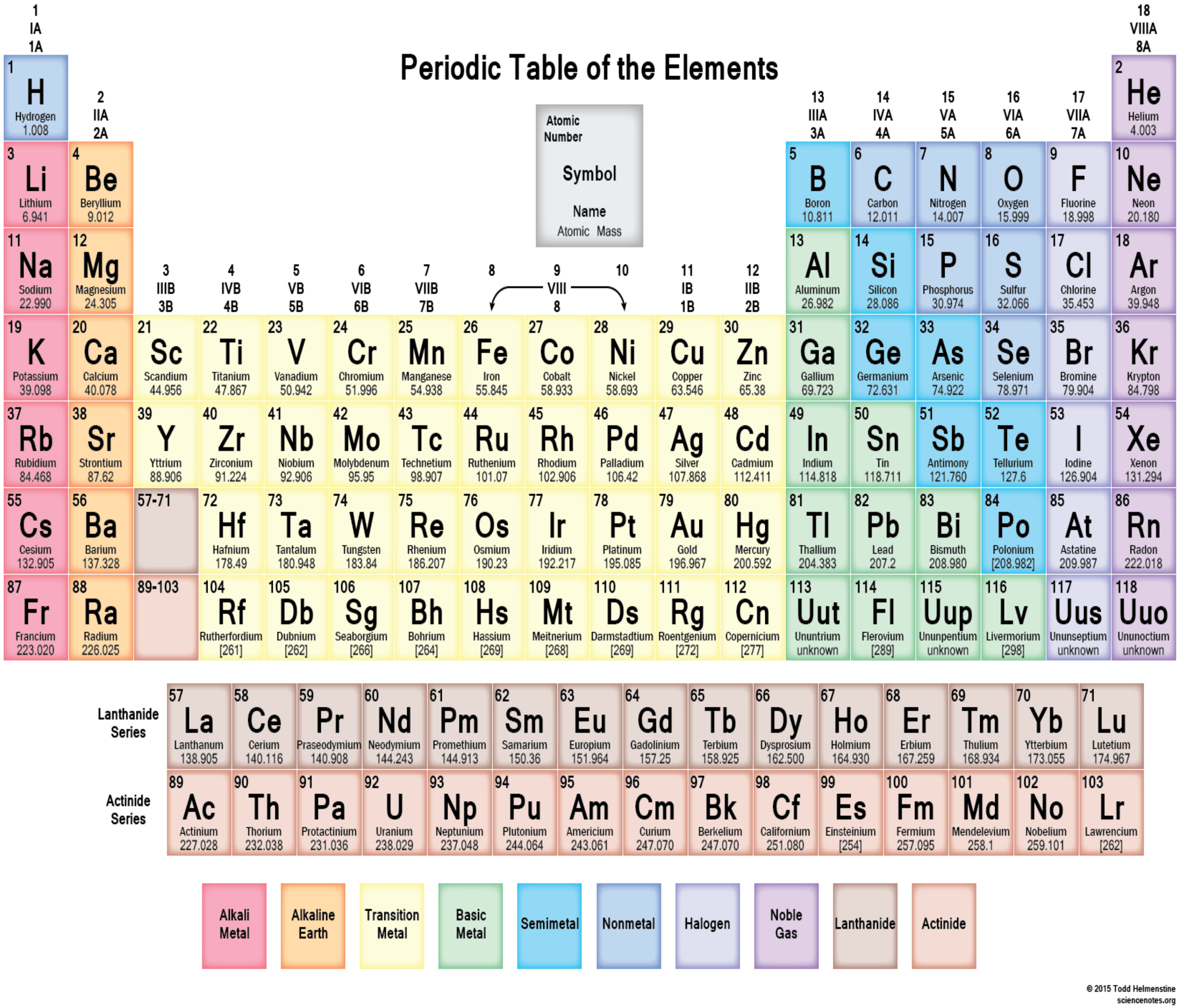


Periodic Table of the Elements

Atomic Number
Symbol
Name
Atomic Mass

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal
Alkaline Earth
Transition Metal
Basic Metal
Semimetal
Nonmetal
Halogen
Noble Gas
Lanthanide
Actinide

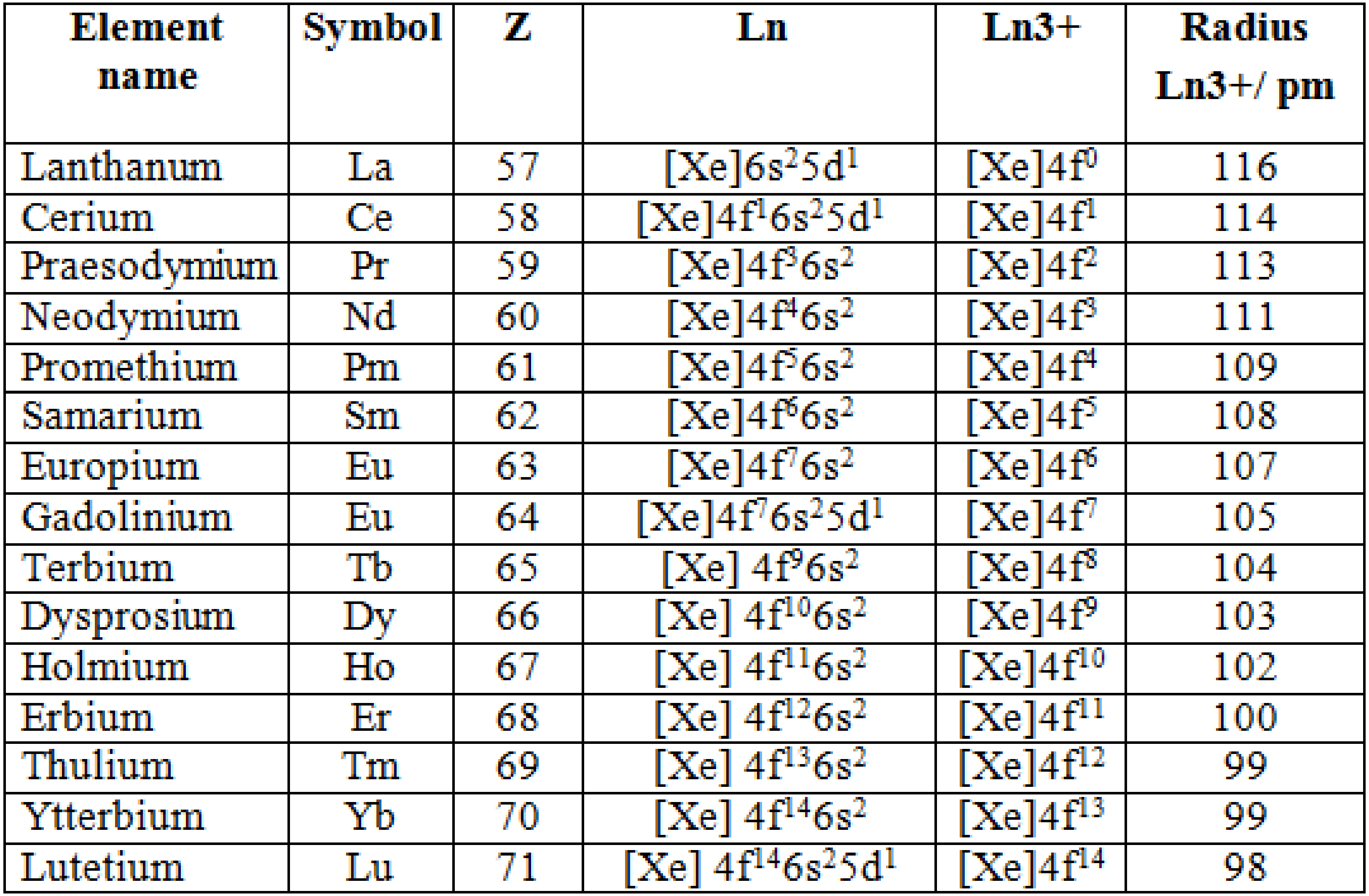
INNER TRANSITION ELEMENTS

The elements in which the additional electron enters (n-2)f orbitals are called inner transition elements.

The valence shell electronic configuration of these elements can be represented as $(n – 2)f^{0-14}(n – 1)d^{0-1}ns^2$.

4f inner transition metals are known as lanthanides because they come immediately after lanthanum and 5f inner transition metals are known as actinoids because they come immediately after actinium.

Electronic Configuration



Element name	Symbol	Z	Ln	Ln3+	Radius Ln3+/ pm
Lanthanum	La	57	$[Xe]6s^{2}5d^{1}$	$[Xe]4f^{0}$	116
Cerium	Ce	58	$[Xe]4f^{1}6s^{2}5d^{1}$	$[Xe]4f^{1}$	114
Praesodymium	Pr	59	$[Xe]4f^{3}6s^{2}$	$[Xe]4f^{2}$	113
Neodymium	Nd	60	$[Xe]4f^{4}6s^{2}$	$[Xe]4f^{3}$	111
Promethium	Pm	61	$[Xe]4f^{5}6s^{2}$	$[Xe]4f^{4}$	109
Samarium	Sm	62	$[Xe]4f^{6}6s^{2}$	$[Xe]4f^{5}$	108
Europium	Eu	63	$[Xe]4f^{7}6s^{2}$	$[Xe]4f^{6}$	107
Gadolinium	Eu	64	$[Xe]4f^{7}6s^{2}5d^{1}$	$[Xe]4f^{7}$	105
Terbium	Tb	65	$[Xe]\ 4f^{9}6s^{2}$	$[Xe]4f^{8}$	104
Dysprosium	Dy	66	$[Xe]\ 4f^{10}6s^{2}$	$[Xe]4f^{9}$	103
Holmium	Ho	67	$[Xe]\ 4f^{11}6s^{2}$	$[Xe]4f^{10}$	102
Erbium	Er	68	$[Xe]\ 4f^{12}6s^{2}$	$[Xe]4f^{11}$	100
Thulium	Tm	69	$[Xe]\ 4f^{13}6s^{2}$	$[Xe]4f^{12}$	99
Ytterbium	Yb	70	$[Xe]\ 4f^{14}6s^{2}$	$[Xe]4f^{13}$	99
Lutetium	Lu	71	$[Xe]\ 4f^{14}6s^{2}5d^{1}$	$[Xe]4f^{14}$	98

Occurrence

- Major sources of lanthanides are Monazite sandcomposed of phosphates of thorium, cerium, neodymium and lanthanum
- Bastnaesite, found in USA and Madagascar is a mixed fluorocarbonate $M^{III}CO^{3}F$ where M is La or the lanthanide metals. It provides 20% total supply of lanthanides.
- The only lanthanide that does not occur naturally is promethium, which is made artificially by near reaction.

Extraction and Separation of Lanthanides

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

Extraction and Separation of Lanthanides

- Reduction of their Trihalides: La, Ce, Pr, Nd and Gd may be obtained by reduction of their trichlorides with calcium at about 1000ºC in an argon filled vessel e.g.
- $2PrCl_3 + 3Ca \xrightarrow{\qquad} 3CaC_{l2} + 2Pr$
- The heavier Ln like Tb, Dy, Ho, Er and Tm can also be obtained by this method but the trifluorides is used, since their trichloride is volatile.

- Also since the heavier Ln have higher melting points and so require a temperature of 1400^{o}C. At this temperature $CaCl_2$ boils. Li is sometimes used instead of Ca.
- $2HoF_3 + 3Ca \rightarrow 3CaF_2 + 2Ho$
- Eu, Sm and Yb are obtained by chemical reduction of their trioxides.

Ion Exchange

- The basis of the lanthanide series separation on an ion exchange column is their ability to form complex ions.
- All lanthanides form +3 ions, M^{+3} whose ionic radii decrease progressively with increasing atomic number from Ce^{+3} to Lu^{+3}.
- As a solution containing +3 lanthanides ions is placed at the top of a column of cation exchange resin[e.g. is Dowex-50 made of a sulphonated polystyrene and contains functional groups $–SO_3H$.] The Ln^{+3} ions are absorbed into the resin and an equivalent amount of hydrogen ions are released from the column

$$Ln^{+3}_{(aq)} + \underset{\text{Cation Exchanger}}{3H^{+}R^{-}_{(s)}} \longrightarrow Ln^{+3}(R^{-})_{(s)} + 3H^{+}_{(aq)}$$

- A citrate buffer (citric acid/ammonium citrate) solution (which complexes with the lanthanide ions) is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution.
- Since the smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column.
- By the correct choice of conditions the lutetium ion, Lu^{+3} (aq), emerges first from the column, followed by the cations ytterbium, thulium, erbium, etc, in order of increasing ionic radius. By using a long ion exchange column, the elements may be obtained at 99.9% with one pass.

Valency Change

- The different properties of the various oxidation states makes separation very easy [ie the properties of Ln^{+4} and Ln^{+2} are very different from that of Ln^{+3}].
- Cerium can be separated from Ln mixtures because it is the only one which has a Ln^{+4} ions stable in aqueous solution.
- A solution containing mixture of Ln^{+3} ions can be oxidized with NaOCl under alkaline conditions to produce Ce^{+4}. Because of the higher charge, Ce^{+4} is much smaller and less basic than Ce^{+3} or any other Ln^{+3}.
- The Ce^{+4} is separated by carefully controlled precipitation of CeO_2 or $Ce(IO_3)_4$, leaving the trivalent ions in solution.

- Also, Eu^{2+} can be separated from a mixture of Ln^{+3}.
- If a solution of Ln^{+3} ions is reduced electrolytically using a Hg cathode or Zn amalgam, then Eu^{2+} is produced.
- If H_2SO_4 is present, $EuSO_4$ which is insoluble will precipitate. This can be filtered off.
- Other methods are Solvent Extraction, Precipitation, Thermal reaction, Fractional crystallization, Complex formation.

ATOMIC AND IONIC SIZES:

THE LANTHANIDE CONTRACTION

The lanthanide contraction is the greater than expected decrease in ionic radii of the elements in the lanthanide series

As the atomic number increases, each succeeding element contains one more electron in the 4f orbital and one proton in the nucleus. The 4f electrons are ineffective in screening the outer electrons from the nucleus causing imperfect shielding. As a result, there is a gradual increase in the nucleus attraction for the outer electrons. Consequently gradual decrease in size occur. This is called lanthanide contraction.

Consequences of Lanthanide Contraction

Following points will clearly depict the effect of lanthanide contraction:

1. Atomic and ionic size: In general the atomic size of a group increases with an increase in atomic number. This increase in size is due to the addition of a new shell. But this trend is not followed by all the groups of the transition series due to lanthanide contraction. The effect of lanthanide contraction cancels the expected increase in atomic size.

Consequently, the atomic radii of the elements of 3rd transition series become almost equal to those of the elements of the 2nd transition series.

Due to the similarity in the size of the elements of the two series, the elements of 2nd and 3rd series resemble each other more closely that do the elements of the 1st and 2nd transition series.

2. Basicity of oxides and hydroxides:

There is a decrease in basic strength of the hydroxides of lanthanides with increase in atomic number. Thus, $La(OH)_3$ is the most basic while $Lu(OH)_3$ is the least basic.

Due to lanthanide contraction, the decrease in size of M^{3+} cations increases the covalent character(i.e, decrease in ionic character) between the M^{3+} ion and OH^- ion(according to Fajan's rules), thereby reducing the basic character of the lanthanide hydroxides.

3. Density: A reduction in the atomic and ionic size of the element causes an increase in the value of density. So it can be concluded that due to lanthanide contraction there is an abnormal increase in the density of these elements

4. Ionization potential: The values of ionization potential should be lower and should decrease regularly down the group. But due to lanthanide contraction there is no trend seen in the values of ionization potential of transition elements, this irregularity occurs after the element tungsten.

Magnetic and Spectral Properties

Lanthanides have very high magnetic susceptibilities due to their large numbers of unpaired f-electrons. The lanthanoid ions other then the f^0 type (La^{3+} and Ce^{3+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to the maximum in neodymium.

Lanthanides have very high magnetic susceptibilities due to their large numbers of unpaired f-electrons.

The strongest known magnets contain lanthanides (eg. Nd-Fe-B, Sm-Fe-N, and Sm-Co).

Lanthanide complexes are used in MRI (medical resonance imaging), eg. $[Gd(III)(dtpa)]^{2-}$

OXIDATION STATES

Predominantly +3 oxidation state.

Occasionally +2 and +4 ions in solution or in solid compounds are also obtained.

This irregularity arises mainly from the extra stability of empty, half filled or filled f subshell.

Luminescence of Lanthanoid Complexes

- Irradiation of some Lanthanide(III) complexes with UV light causes them to fluoresce
- The origin of fluorescence is 4*f*-4*f transitions*.
- The excited state produced decays to the ground state with emission of energy.
- Some examples are Eu^{3+} (red) and Tb^{3+} (green)
- They can be used as phosphors in television sets and fluorescent lighting.
- These applications are specific to lanthanoid ions because of the sharp transitions observed.

Properties

- Silvery white soft metals, tarnish in air rapidly
- Hardness increases with increasing atomic number, samarium being steel hard.
- Good conductor of heat and electricity.

Chemical Properties

- Metal combines with water to form hydroxides.
- The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.
- They liberate hydrogen from dilute acids and burn in halogens to form halides.
- They form oxides and hydroxides, Ln_2O_3 and $Ln(OH)_3$, basic like alkaline earth metal oxides and hydroxides.
- Forms sulphides and nitrides when heated in sulphur and nitrogen respectively.

Organometallic compounds

- The organometallic compounds of the lanthanoids are dominated by good donor ligands, with complexes of acceptor ligands being rare.

  This is attributed to

- The lack of orbitals because the 5d orbitals are empty and the 4f orbitals are buried so this restricts the number of bonding modes that are available to the lanthanoid ions.
- The strong electropositive nature of the lanthanoids means they need good donor(eg alkoxide, amide and halide ligands which are both σ and π donors), not good acceptor ligands(eg CO and phosphine ligands which are both σ donors and π acceptors)

- The bonding in the organometallic lanthanoid complex that do form is predominantly ionic and governed by electrostatic factors and steric requirements
- All organometallic complexes are strong Lewis acids and are very sensitive to air and moisture.
- Examples of organometallic lanthanoid compounds:

  $Ln(Cp)_3$ compounds (Cp-cyclopentadienyl compounds)

  $Sm(\eta 5\text{-}Cp^*)_3$ $Sm(\eta 1\text{-}Cp^*)(\eta 5\text{-}Cp^*)_2$

  this exists in equilibrium

These complexes contain Ln^{3+} ion with a limited number of Ln^{2+} compounds.

σ-Bonded alkyl groups are common with compounds containing cyclopentadienyl ligands tending to dominate.

Cp groups are electrostatistically bound to a central cation.

Other examples are η_8- Cyclooctatetraene ligands eg $Ce(C_8H_8)_2$.

Uses

Best single use of the lanthanoids is for the production of alloy steels for plates and pipes.

A well known alloy is misch metal which consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. A good deal of misch metal is used in Mg based alloy to produce bullets, shell and lighter flint.

2. Use as catalysts: Lanthanide catalysts have been repeatedly recommended for use in numerous organic reactions, including the hydrogenation of ketones to form secondary alcohols, the hydrogenation of olefins to form alkanes, the dehydrogenation of alcohols and butanes, and the formation of polyesters.

3 . Use in the glasses industry:

- Cerium oxide has been found to be a rapid polishing agent for glass and are used in the polishing of lenses for cameras, binoculars, and eyeglasses, as well as in polishing mirrors and television faceplates.

- Neodymium is added to some glasses to counteract the yellowish tint caused by iron impurities. Very pure neodymium oxide, when added in sufficient quantities (1–5 percent), gives a beautiful purple glass.
- Praseodymium and neodymium are added to glass to make welders‘ goggles, that absorb the bright-yellow light from the sodium flame. The same combination is sometimes added to the glass used in television faceplates to decrease the glare from outside light sources.
- Cerium oxide increases the opacity of white porcelain enamels.

4. Use in the metallurgical industry:

Small amounts of misch metal and cerium have long been added to other metals or alloys to remove their nonmetallic impurities. Misch metal added to cast iron makes a more malleable iron. Added to some steels, it makes them less brittle. The addition of misch metal to certain alloys has been reported to increase the tensile strength and improve the hot workability and the high-temperature oxidation resistance. The flints of cigarette lighters are an alloy of misch metal and iron. The addition of misch metal or pure rare-earth elements to magnesium increases its high-temperature strength and its creep resistance—that is, resistance to slow deformation under prolonged use.

5. Use in the television industry:

It has been found that if a small amount of europium oxide (Eu_2O_3) is added to yttrium oxide (Y_2O_3), it gives a brilliant-red phosphor. Colour television screens utilize red, green, and blue phosphors. In the past, a zinc–cadmium sulfide was used as the red phosphor, but it was not completely satisfactory because its fluorescent band was too wide, and it could not be made to fluoresce as intensely as the other phosphors. The Y_2O_3–Eu_2O_3 phosphor corrected these disadvantages and made possible much brighter and more natural coloured picturesoxide. The rare-earth phosphors are also finding use in mercury-arc lights, which are used for sporting events and special street lighting. Instead of the unhealthy-looking blue light of the mercury arc, the phosphors give an intense white radiation similar to daylight.

- Other applications: Another significant industrial application of rare earths is in the manufacture of strong permanent magnets.
- Alloys of cobalt with rare earths, such as cobalt–samarium, produce permanent magnets that are far superior to most of the varieties now on the market.
- Another relatively recent development is the use of a barium phosphate–europium phosphor in a sensitive X-ray film that forms satisfactory images with only half the exposure.
- Europium, gadolinium, and dysprosium have large capture cross sections for thermal neutrons—that is, they absorb large numbers of neutrons per unit of area exposed. These elements, therefore, are incorporated into control rods used to regulate the operation of nuclear reactors or to shut them down should they get out of control.

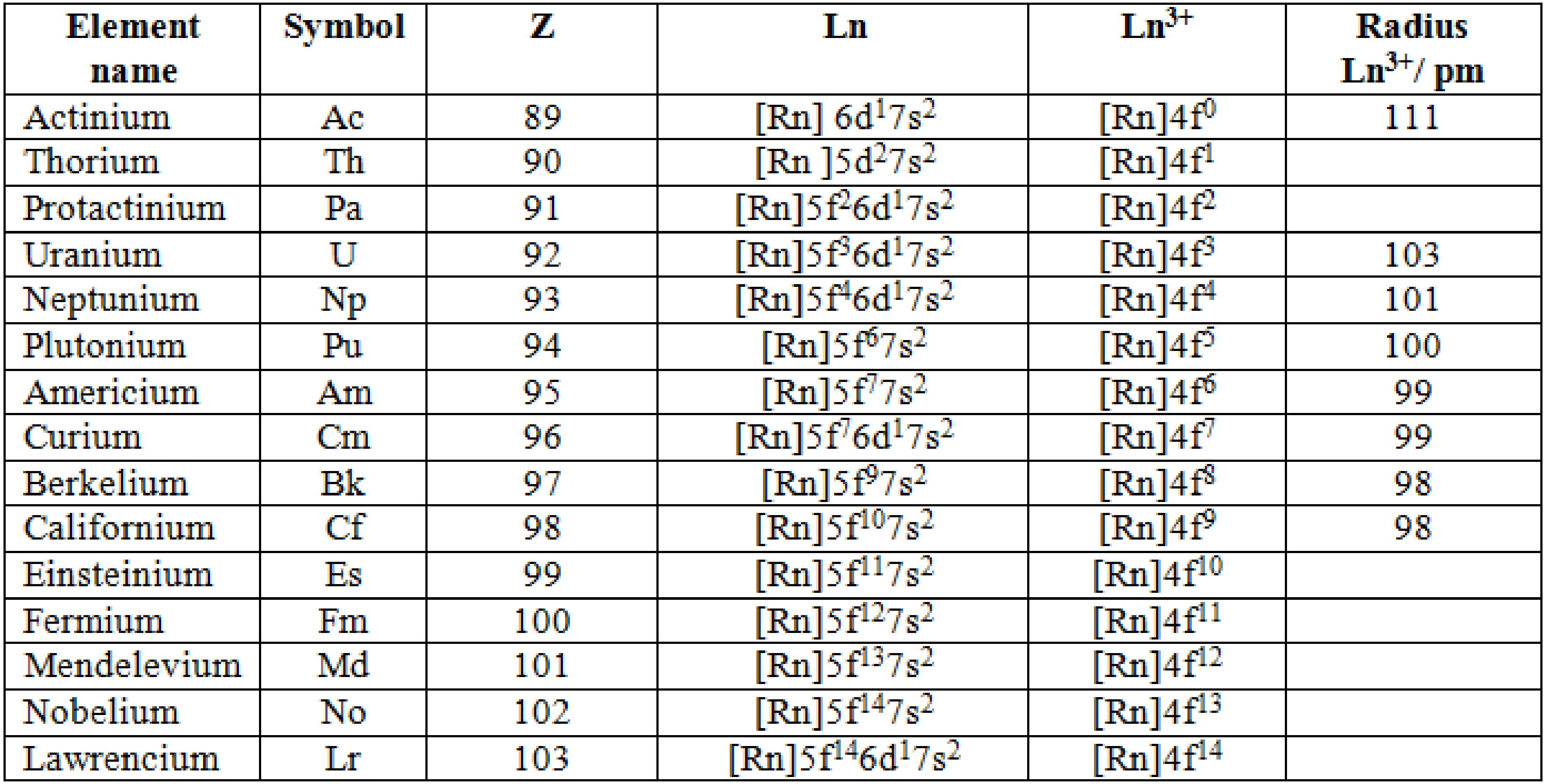
The Actinides

- Result from the filling of the 5f orbitals.
- All isotopes are radioactive, with only ^{232}Th, ^{235}U, ^{238}U and ^{244}Pu having long half-lives.
- Only Th and U occur naturally-both are more abundant in the earth’s crust than tin.
- The others must be made by nuclear processes.

Some Characteristic Properties of Actinides

- The dominant oxidation state of actinides is +3. Actinides also exhibit an oxidation state of +4. Some actinides such as uranium, neptunium and plutonium also exhibit an oxidation state of +6.
- The actinides show actinide contraction (like lanthanide contraction) due to poor shielding of the nuclear charge by 5f electrons.
- All the actinides are radioactive. Actinides are radioactive in nature. So the study of their chemistry is difficult in the laboratory. Their chemistry is studied using tracer techniques.

Electronic Configuration



Element name	Symbol	Z	Ln	Ln^{3+}	Radius Ln^{3+}/ pm
Actinium	Ac	89	[Rn] $6d^1 7s^2$	[Rn]$4f^0$	111
Thorium	Th	90	[Rn]$5d^2 7s^2$	[Rn]$4f^1$	
Protactinium	Pa	91	[Rn]$5f^2 6d^1 7s^2$	[Rn]$4f^2$	
Uranium	U	92	[Rn]$5f^3 6d^1 7s^2$	[Rn]$4f^3$	103
Neptunium	Np	93	[Rn]$5f^4 6d^1 7s^2$	[Rn]$4f^4$	101
Plutonium	Pu	94	[Rn]$5f^6 7s^2$	[Rn]$4f^5$	100
Americium	Am	95	[Rn]$5f^7 7s^2$	[Rn]$4f^6$	99
Curium	Cm	96	[Rn]$5f^7 6d^1 7s^2$	[Rn]$4f^7$	99
Berkelium	Bk	97	[Rn]$5f^9 7s^2$	[Rn]$4f^8$	98
Californium	Cf	98	[Rn]$5f^{10} 7s^2$	[Rn]$4f^9$	98
Einsteinium	Es	99	[Rn]$5f^{11} 7s^2$	[Rn]$4f^{10}$	
Fermium	Fm	100	[Rn]$5f^{12} 7s^2$	[Rn]$4f^{11}$	
Mendelevium	Md	101	[Rn]$5f^{13} 7s^2$	[Rn]$4f^{12}$	
Nobelium	No	102	[Rn]$5f^{14} 7s^2$	[Rn]$4f^{13}$	
Lawrencium	Lr	103	[Rn]$5f^{14} 6d^1 7s^2$	[Rn]$4f^{14}$	

Physical and Chemical Reactivity

- Silvery in appearance but display a variety of structures due to the irregularity in metallic radii which are far greater than are found in lanthanoids.
- Highly reactive metals, especially when finely divided.
- Action of boiling water gives mixture of oxides and hydroxides.
- Combination with most non-metals takes place at moderate temperature.
- HCl attacks all metals but most are slightly affected by HNO_3 owing to the formation of protective oxide layers.
- Alkalies have no effect.

Comparison of Lanthanides and Actinides Similarities

- Lanthanides and actinides involve filling of f-orbitals and thus are similar in many respects.
- The most common oxidation state is +3 for both lanthanides and actinides.
- Both are electropositive in nature and thus very reactive.
- Magnetic and spectral properties are exhibited by both lanthanides and actinides.
- Actinides exhibit actinide contraction just like lanthanides.

DIFFERENCES

- Besides +3, lanthanides also show oxidation states of +2 and +4 while actinides show higher oxidation states of +4, +5, +6 and + 7 as well.
- Lanthanide ions are light coloured while most of the actinide ions are coloured.
- Actinides have a greater tendency towards complex formation as compared to lanthanides.

- Lanthanide compounds are less basic while actinide compounds have appreciable basicity
- Almost all actinides are radioactive while lanthanides, except promethium, are non-radioactive.
- The magnetic properties of actinides can be easily explained while it is difficult to do so in the case of lanthanides.

Thank you!