Theoretical Inorganic Chemistry Second year Class

Representative and Lanthanides Elements

Prepared by Assistant Professor -

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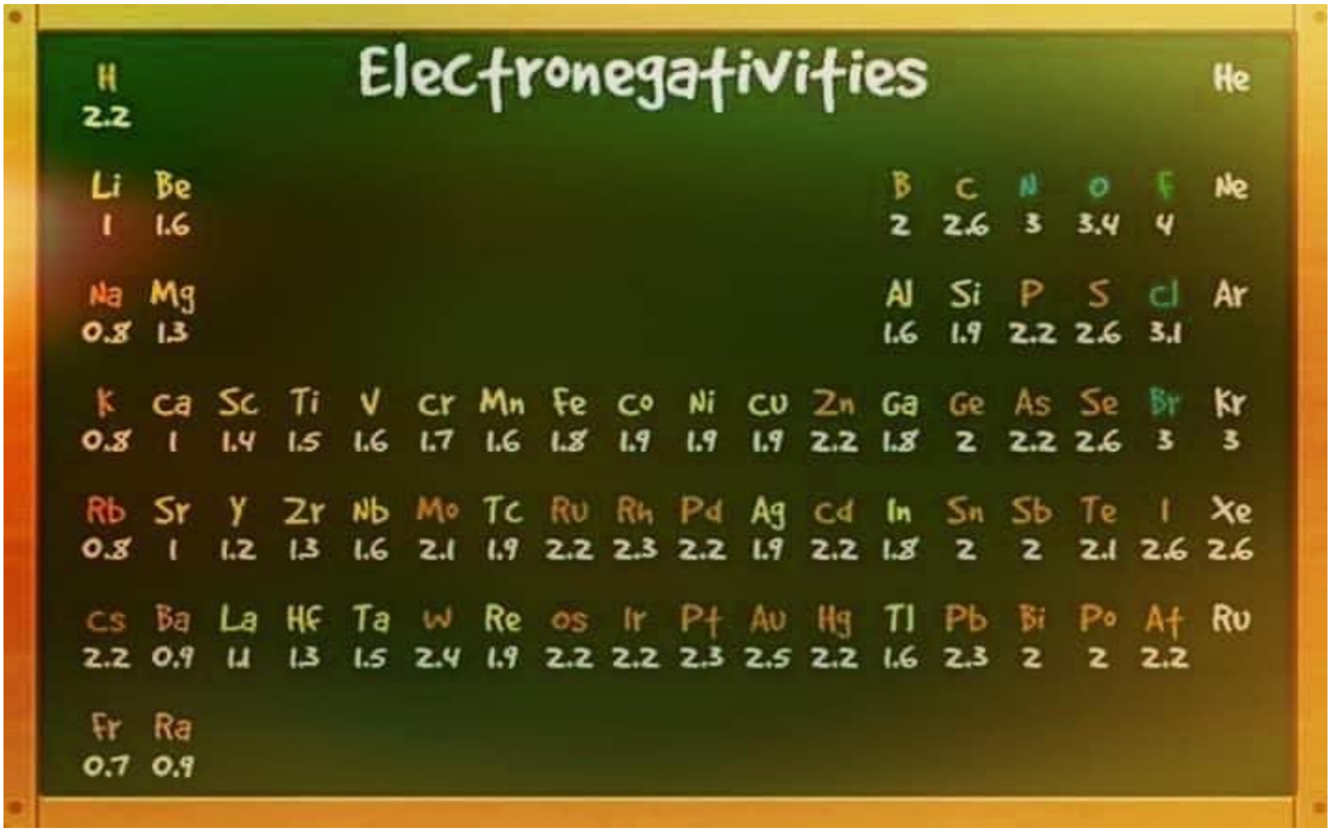
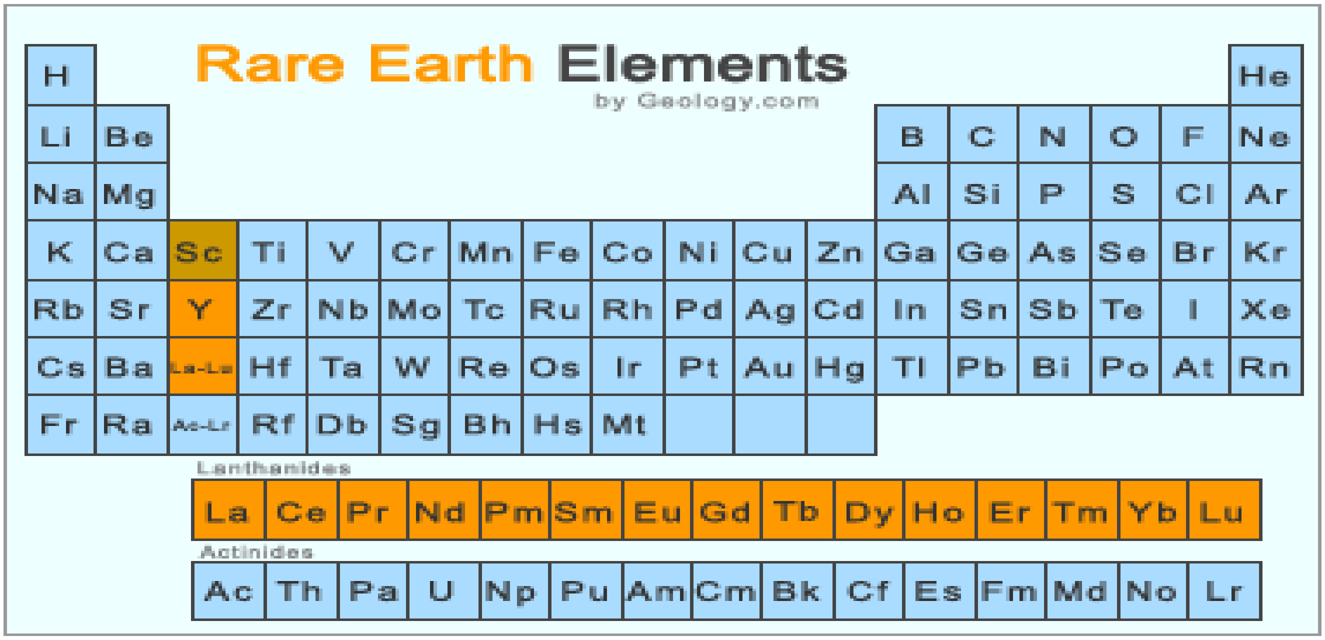


Electronegativities

H																	He
2.2																	
Li	Be											B	C	N	O	F	Ne
1	1.6											2	2.6	3	3.4	4	
Na	Mg											Al	Si	P	S	cl	Ar
0.8	1.3											1.6	1.9	2.2	2.6	3.1	
K	ca	Sc	Ti	V	cr	Mn	Fe	co	Ni	cu	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1	1.4	1.5	1.6	1.7	1.6	1.8	1.9	1.9	1.9	2.2	1.8	2	2.2	2.6	3	3
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	cd	In	Sn	Sb	Te	I	Xe
0.8	1	1.2	1.3	1.6	2.1	1.9	2.2	2.3	2.2	1.9	2.2	1.8	2	2	2.1	2.6	2.6
cs	Ba	La	Hf	Ta	W	Re	os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Ru
2.2	0.9	1.1	1.3	1.5	2.4	1.9	2.2	2.2	2.3	2.5	2.2	1.6	2.3	2	2	2.2	
Fr	Ra																
0.7	0.9																

2022-2023



Rare Earth Elements

by Geology.com

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt									

Lanthanides

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Actinides

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Rare earth elements (REE) are naturally occurring materials with unique properties that make them essential to new technologies. REEs include 17 elements that share similar chemical properties, which give them the ability to discharge and accept electrons, making them an integral component of many modern day electronic, optical, magnetic,and catalytic uses.

These-elements include: Scandium, Yttrium, Lanathanum, Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Holmium, Dysprosium, Erbium, Thulium, Ytterbium, Lutetium.

Rare earth elements work best when they are added in small doses to composites and alloys. They have unique chemical and physical properties that allow them to interact with other elements and get results that neither element could get on its own.

Despite their name, REEs are actually commonly found on the Earth, but most do not occur in large enough quantities and high enough concentrations to mine easily.

Origins

Rare earth elements were discovered in 1787 by Swedish Army Lieutenant Carl Axel. They were first commercially produced in the 1880s when they were mined in Sweden and Norway. The first foreign production was in Brazil in 1887, and India began producing them in 1911.

From 1940 to 1990, the United States produced and mined its own rare earth minerals. Mountain Pass mine in California was the biggest resource in the country.

Until the 1980s the U.S. was one of the world's largest producers. China has increased production by more than 500% since 1990 due to its substantial deposits and cheap labor.

Processing

Rare earths are difficult to mine because they aren't found in large quantities or veins like other minerals such as gold. They need to be separated from one another using a variety of mining and processing techniques.

There are three main methods for separating and refining the elements including: Fractional Crystallization, Ion-Exchange, Liquid-Liquid Extraction, or Solvent Extraction.

Most REE mines only produce these types of elements using large-scale techniques that involve drilling, blasting, and hauling.

The elements are separated and purified and then refined to meet industry standards for the proper applications.

Uses

These 17 elements are important to the manufacture of many high technology products. In fact, many of the things you use every day would not exist without REEs.

Neodymium- is used to make powerful magnets used in loud speakers and hard drives as well as hybrid cars.

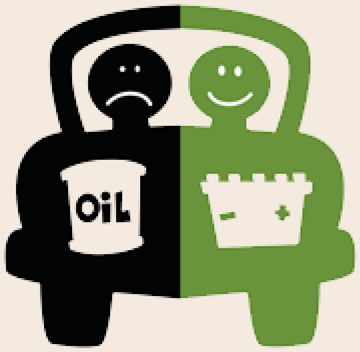
Lanthanum -is used in camera and telescopic lenses, as well as studio lighting and cinema projection

Cerium- is used in catalytic converters in cars, as well as refining crude oil.

Praseodymium -is used to create strong metals for use in aircraft engines. It is also used to make visors to protect welders and glassmakers.

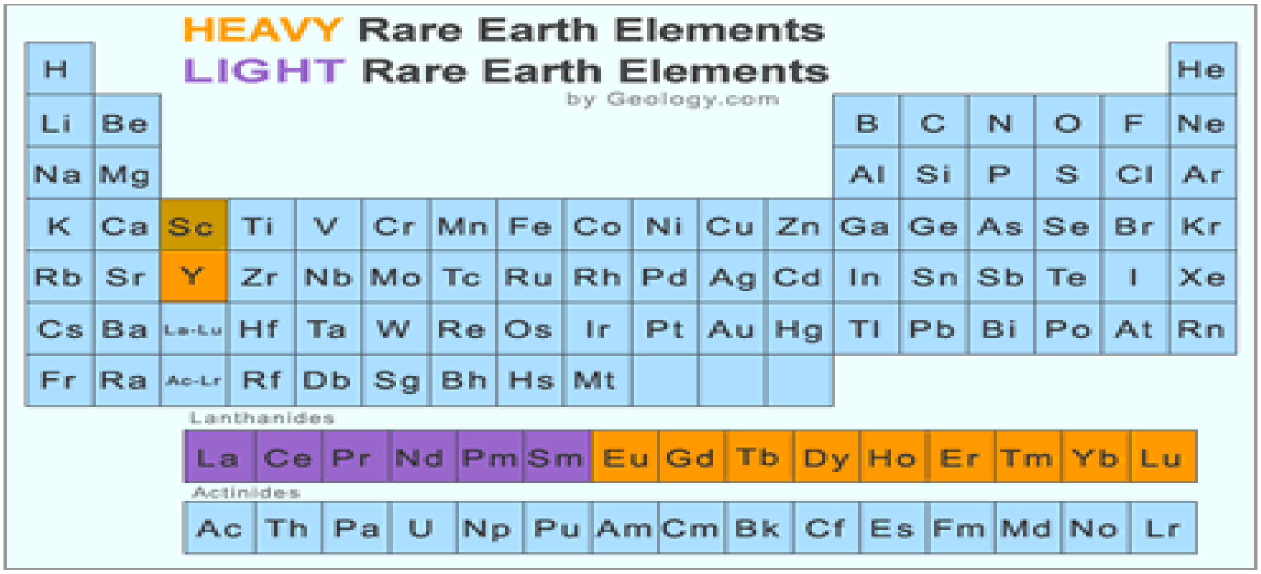
Gadolinium- is used in X-ray and MRI scanning systems, as well as television screens.

Yttrium, terbium, and europium are important for television and computer screens, as well as other devices with visual displays.



Every hybrid-electric and electric vehicle has a large battery. Each battery is made using several pounds of rare earth compounds. The use of electric vehicles is expected to increase rapidly, driven by energy independence, climate change and other concerns. This will increase the demand for rare earth materials.

Tiny amounts of rare earth metals are used in most small electronic devices. These devices have a short lifespan, and REE recycling is infrequently done. Billions are thrown away each year.



HEAVY Rare Earth Elements
LIGHT Rare Earth Elements
by Geology.com

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt									

Lanthanides

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Actinides

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Heavy and light rare earth elements: The rare earth elements are often subdivided into "Heavy Rare Earths" and "Light Rare Earths." Lanthanum, cerium, praseodymium, neodymium, promethium, and samarium are the "light rare earths." Yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium are the "heavy rare earths." Although yttrium is lighter than the light rare earth elements, it is included in the heavy rare earth group because of its chemical and physical associations with heavy rare earths in natural deposits.

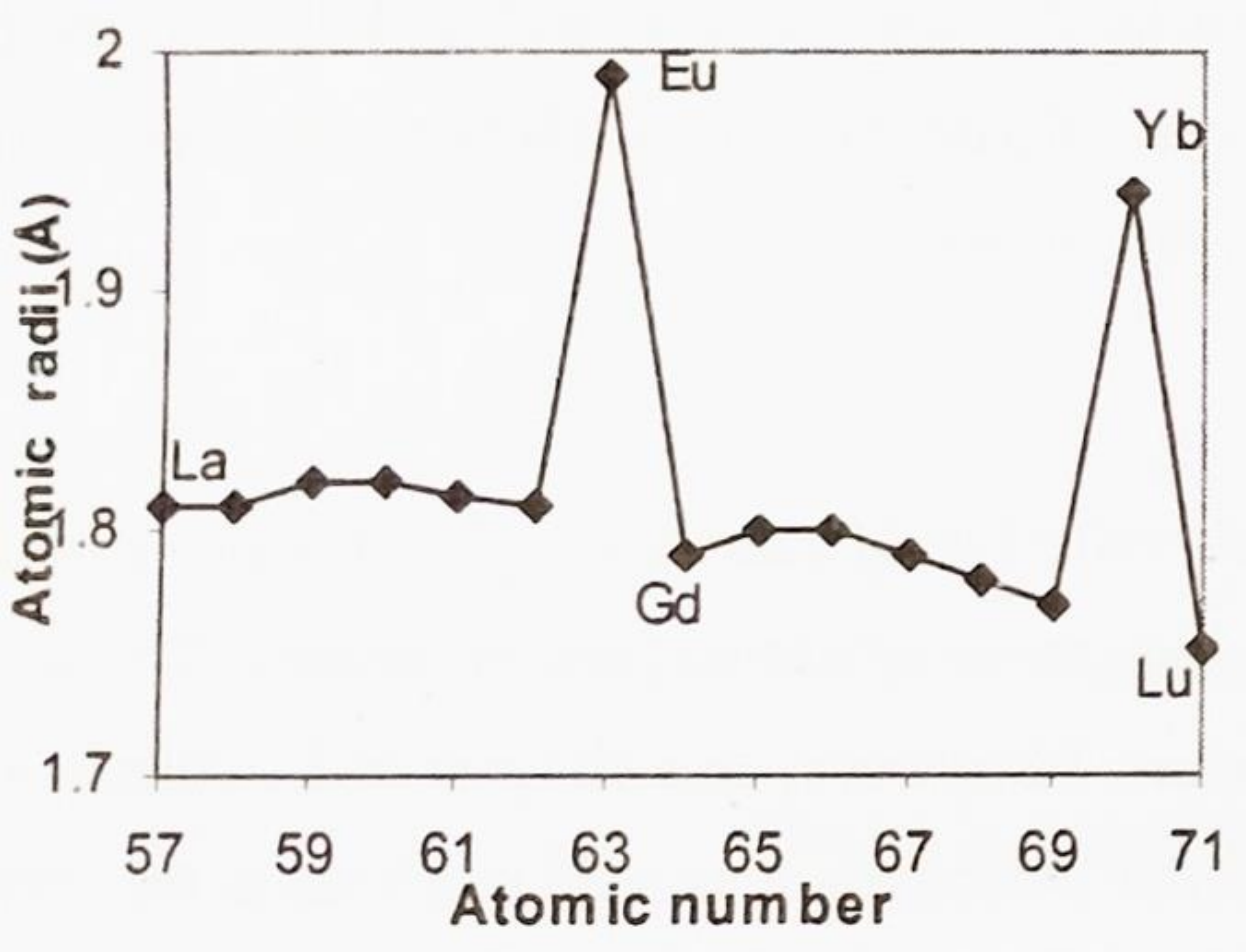
Shielding and Lanthanide Contraction

As a result of the poor shielding of the 4f electrons there is a steady (fixed) increase in effective nuclear charge and related reduction in atomic size . Although his trend is apparent from the atomic radii .

The Lanthanide Contraction describes the atomic radius trend that the Lanthanide series exhibit. Another important feature of the Lanthanide Contraction refers to the fact that the 5s and 5p orbitals penetrate the 4f sub-shell so the 4f orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease. This decrease in size continues throughout the series.

Introduction

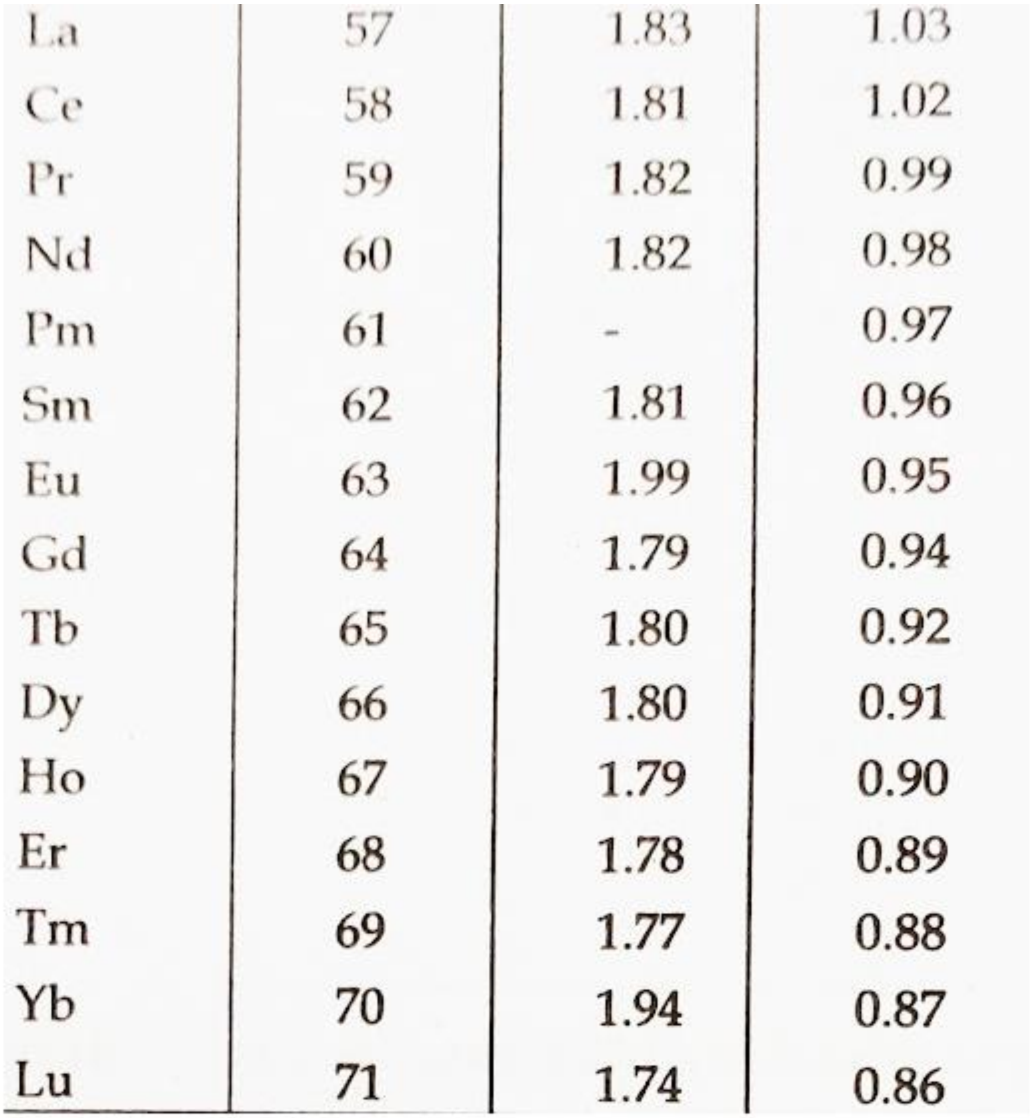
The Lanthanide Contraction applies to all 14 elements included in the Lanthanide series. This series includes Cerium(Ce), Praseodymium(Pr), Neodymium(Nd), Promethium(Pm), Samarium(Sm), Europium(Eu), Gadolinium(Gd), Terbium(Tb), Dysprosium(Dy), Holmium(Ho), Erbium(Er), Thulium(Tm), Ytterbium(Yb), and Lutetium(Lu). The atomic radius, as according to the Lanthanide Contraction, of these elements decreases as the atomic number increases. We can compare the elements Ce and Nd by looking at a periodic table. Ce has an atomic number of 58 and Nd has an atomic number of 60. Which one will have a smaller atomic radius? Nd will because of its larger atomic number.



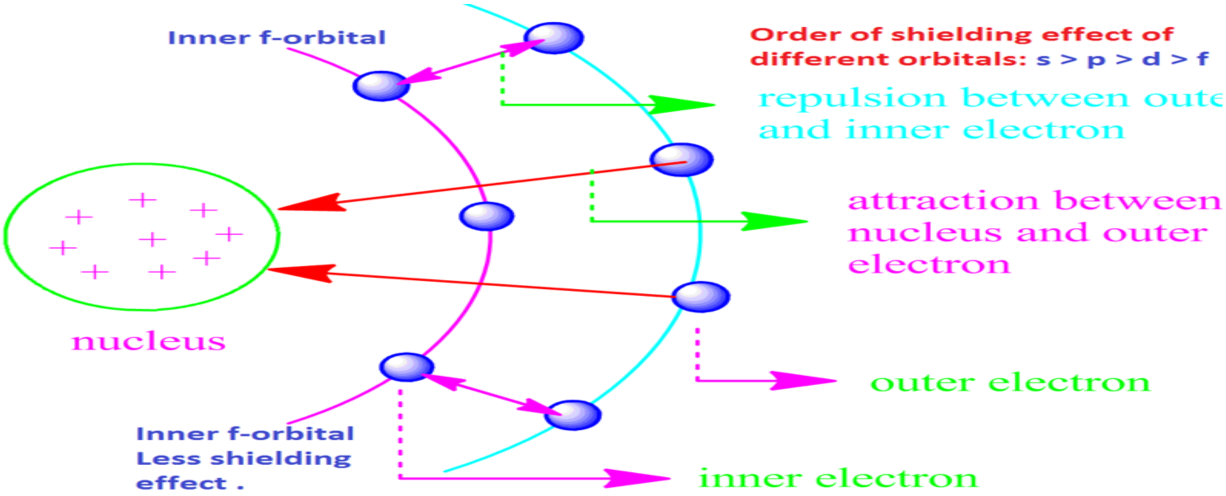
the graph shows the atomic radius decreasing as the atomic number is increasing, Lanthanide Contraction.

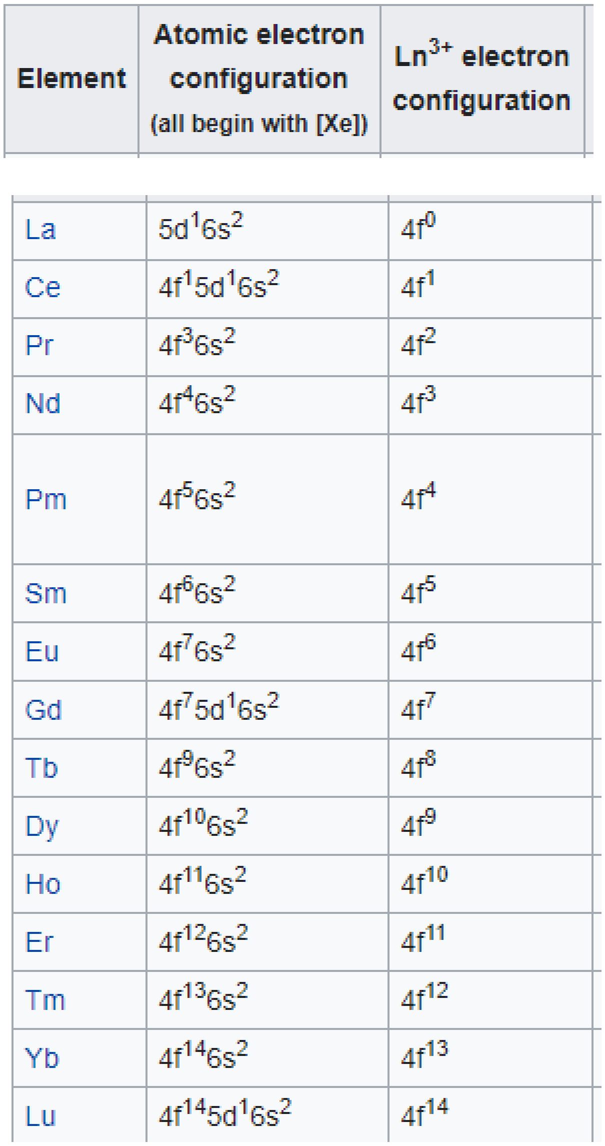
Variation of atomic and ionic radii of lanthanides

Element	Atomic number	Atomic radii (Å)	Ionic radii of Ln^{3+} ions (Å)



La	57	1.83	1.03
Ce	58	1.81	1.02
Pr	59	1.82	0.99
Nd	60	1.82	0.98
Pm	61	-	0.97
Sm	62	1.81	0.96
Eu	63	1.99	0.95
Gd	64	1.79	0.94
Tb	65	1.80	0.92
Dy	66	1.80	0.91
Ho	67	1.79	0.90
Er	68	1.78	0.89
Tm	69	1.77	0.88
Yb	70	1.94	0.87
Lu	71	1.74	0.86



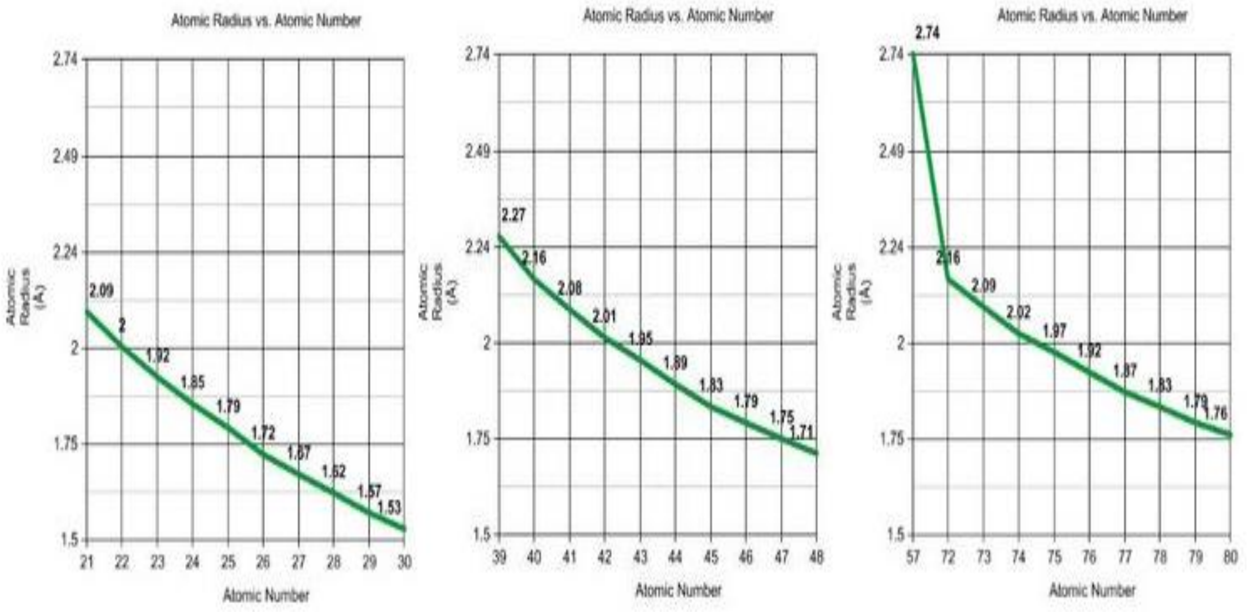


Element	Atomic electron configuration (all begin with [Xe])	Ln^{3+} electron configuration
La	$5d^1 6s^2$	$4f^0$
Ce	$4f^1 5d^1 6s^2$	$4f^1$
Pr	$4f^3 6s^2$	$4f^2$
Nd	$4f^4 6s^2$	$4f^3$
Pm	$4f^5 6s^2$	$4f^4$
Sm	$4f^6 6s^2$	$4f^5$
Eu	$4f^7 6s^2$	$4f^6$
Gd	$4f^7 5d^1 6s^2$	$4f^7$
Tb	$4f^9 6s^2$	$4f^8$
Dy	$4f^{10} 6s^2$	$4f^9$
Ho	$4f^{11} 6s^2$	$4f^{10}$
Er	$4f^{12} 6s^2$	$4f^{11}$
Tm	$4f^{13} 6s^2$	$4f^{12}$
Yb	$4f^{14} 6s^2$	$4f^{13}$
Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$

Shielding and its Effects on Atomic Radius

The Lanthanide Contraction is the result of a poor shielding effect of the 4f electrons. The shielding effect is described as the phenomenon by which the inner-shell electrons shield the outer-shell electrons so they are not effected by nuclear charge. So when the shielding is not as good, this would mean that the positively charged nucleus has a greater attraction to the electrons, thus decreasing the atomic radius as the atomic number increases. The s orbital has the greatest shielding while f has the least and p and d in between the two with p being greater than d.

The Lanthanide Contraction can be seen by comparing the elements with f electrons and those without f electrons in the d- block orbital. Pd and Pt are such elements. Pd has 4d electrons while Pt has 5d and 4f electrons. These 2 elements have roughly the same atomic radius. This is due to Lanthanide Contraction and shielding. While we would expect Pt to have a significantly larger radius because more electrons and protons are added, it does not because the 4f electrons are poor at shielding. When the shielding is not good there will be a greater nuclear charge, thus pulling the electrons in closer, resulting in a smaller than expected radius.



Row 1 of Periodic Table d block Row 2 Row 3

The graphs depict the atomic radii of the first three rows of transition metals. We can apply the same principle as applied with the elements Pd and Pt to whole rows and columns. As we can see by comparing Row 1 with Row 2, the atomic radii differ greatly between the elements, but if we compare Row 2 with Row 3, the atomic radii do not have much difference. Elements with atomic number 23 and 41 lie in the same column of the periodic table and have a significantly large difference in atomic radii (atomic radii increases from Row 1 to Row 2), but elements 41 and 73, also in the same column, only differ slightly. This is the cause of introducing 4f electrons in Row 3. In Row 3, we would expect the elements to carry on the same trend as was witnessed between Rows 1 and 2 (large increase in atomic radii) but we do note this is because the 4f orbitals are not doing a great job of shielding.

d- Block Contraction (Scandide Contraction)

The d-block contraction, also known as the Scandide Contraction, describes the atomic radius trend that the d-block elements (Transition metals) experience. Normally the trend for atomic radius, moving across the periodic table is that the atomic radius decreases significantly. In the transition metals with d- electrons as we move from left to right across the periodic table, the element’s atomic radius only decreases slightly. This is because they have the same amount of s-electrons, but are only differing in d-electrons.These d-electrons are in an inner shell (penultimate shell) and electrons are getting added to this shell, another shell is not created. The d- electrons are not good at shielding the nuclear charge, so the atomic radius does not change much as electrons are added. Almost like disregarding the d- electrons being added.

Effects on Ionization Energy and Properties

As the proton number increases and the atomic radius decreases, the ionization energy increases. This is due to a more positively charged nucleus and a greater pull on the electrons by the nucleus. A greater pull is the result of an increased effective nuclear charge. Effective nuclear charge is caused by the nucleus having a more positive charge than the negative charge on the electron (net positive charge). The density, melting point, and hardness increase from left to right throughout the Lanthanide Series. The Lanthanide Contraction makes chemical separation of the Lanthanides easier. The Lanthanide Contraction, while making the chemical separation of Lanthanides easier, it makes the separation of elements following the series a bit more difficult.