



Chemical Periodicity of the Inner Transition Metals

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ABSTRACT

The current studies review the existing literatures about chemical periodicity of inner transitional metals. Chemical properties of inner transition metals have three incomplete outermost nucleus shells and are all metals. In some cases they are quite malleable and ductile. Many lanthanides including Lutetium are used in the lighting industry. Actinides don't occur in nature except for uranium, and are highly unstable. The study discuss on the physical properties and trends in chemical properties of inner transition metals including atomic radius, electron negativity, ionization energy, and reduction potential of inner transition metals.

Keywords: Chemical periodicity; Physical and chemical properties; Inner transition metals

INTRODUCTION

In 1869 and 1870 Dmitri Mendeleev and Lothar Meyer discovered that the properties of elements can be represented as periodic functions of their atomic weigh. This laid the foundation of periodic table. But since the end of the 19th century new elements have been discovered and the form of the periodic table has been significantly modified.

The concept of chemical periodicity is central to study inorganic chemistry [1-3]. Chemical periodicity and the periodic table found their natural interpretation in the detailed electronic structure of the atom and the modern periodic table places elements in the s, p, d and f blocks and in groups 1-18 as follows in below Figure 1.

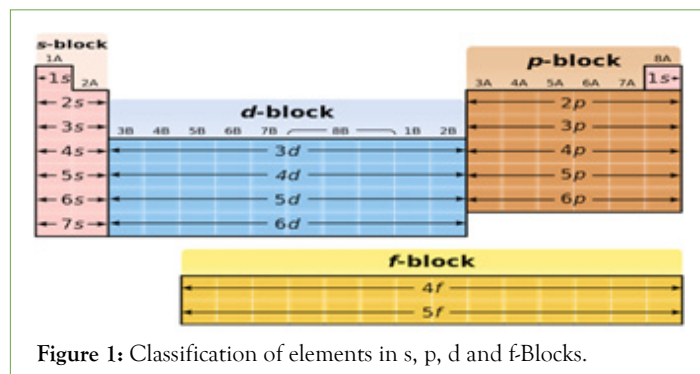


Figure 1: Classification of elements in s, p, d and fBlocks.

Chemical periodicity is thus the consequence of the variation in ground state electronic configurations and many physical and chemical properties follow periodic trends [4].

In this work our objectives aim at describing in summary trends in important physical properties of elements down their respective groups and across their respective periods [5]. Mainly our focus will be on the chemical periodicity of Lanthanides and Actinides [6].

CHEMICAL PERIODICITY DOWN GROUPS AND ACROSS PERIODS IN S, P, AND D-BLOCK

S-block and P-block elements

Trends in atomic radii: The atomic radius is a half distance between the nucleus of an atom and electron in the outermost shell. Within the period the atomic radii decrease from left to right because electrons are added to the same shell and that increases the nuclear attraction and reduces the atomic size [7]. In the group atomic radii increase from top to bottom because the number of energy level increases.

Trends in electronegativity: Electronegativity is a tendency of an atom to attract shared pair of electrons itself. Within a period electronegativity increases from left to right because the positive charges in the nucleus increase with the nuclear attraction of the atom. In the same group electronegativity decreases from the top to the bottom because the energy level increase from the top to bottom.

Trends in ionization energy: Ionization energy is the amount of energy required to remove an electron from neutral gaseous atom. Across the period ionization energy increases with the increase of the nuclear charges, while it decreases down the group due to the increase of the energy level which decrease the nuclear attraction.

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Melting and boiling point: The melting point of an atom is the energy required to change solid substance to liquid while the boiling point refers to the energy required to change a substance from liquid to gas.

- In the left region boiling and melting point decrease down the group due to the decrease of strength of metallic bonds.
- In the right region at extreme right in group 17 and 18 there is increase of melting point down the group.
- From the left to the middle of periodic table there is increase of melting and boiling point from left to right due to the increase of strength of the metallic bond.
- While from the middle left to right there is a decrease of melting and boiling point due the increase of nonmetallic character.

Metallic character: Metallic character refers to the level of reactivity of a metal. The metallic character decreases from left to right as the nuclear attraction increases. Down the group the metallic character increases with the decrease of nuclear attraction.

Electron affinity: Electron affinity is the amount of energy released by an atom or molecule when an electron is added to a neutral atom or molecule in the gaseous state to form a negative ion. Across the period the electron affinity increases from left to right because electron added to the energy level become closer to the nucleus. While in group it decreases from top to bottom because the force of attraction is relatively weaker.

D-block elements

Atomic radius: Across the period atomic radii of the element of a particular series decrease gradually up to the midway element and then these values remain almost constant up to the element of group 11 and then increase. From Sc to Mn the atomic radii decrease. This decrease is caused by gradual increase in nuclear charge with increase in atomic number. In midway elements electron(s) added to 3d orbital screen the 4s electron [8,9]. The attraction between nucleus and 4s decrease. Towards the end of each series there is electron-electron repulsion between electrons being added to 3d orbitals. This increase in repulsion becomes greater than the attraction between the nucleus and the 4s electron. Down the group the atomic radii increases as the atomic number increase.

Reduction potential: The reducing power decreases as reduction potential increase. Element which has high negative E_{red}° is the best reducing agent than element which has less negative E_{red}° (Table 1).

Table 1: Considering the following values of the reduction potential for the 1st transition series of the elements.

Elements	V	Cr	Mn	Fe	Co	Ni	Co
Reduction potential E_{red}° (volts)	-1.18	-0.9	-1.18	-0.4	-0.28	-0.25	0.34

Ionization energy: The values of ionization energy increase as we move from left to right in each series, but this increase is not quite regular. This is due to the increase of the nuclear charge which attracts the ns² electron cloud with greater force. However as the electron is added to (n-1) d sub-shell at each next element, the ns² electrons are shielded more and more. The effect of increasing nuclear charge is opposed the additional screening effect of the nucleus and consequently, the ionization energies increase quite slowly along a given series.

Ionization energy decreases as we move down in group IIIB while in most of remaining groups the ionization energies increase in the same direction. This happens because the ionization energies of the elements lying after La₅₇ in the 3rd series are greater than those of their corresponding elements lying in 1st and 2nd series.

CHEMICAL PERIODICITY OF INNER TRANSITION METALS OR F-BLOCK ELEMENTS

General description of inner-transition elements

Inner-transition metals are located separately at the bottom of the periodic table [7]. The 1st series lies between La₅₇ and Hf₇₂ in the 6th period and it starts with the element Ce₅₈ to Lu₇₁ (14 elements) following La₅₇ which has close similarities with them. These elements are called Lanthanides or Lanthanones. The 2nd series lies between Ac₈₉ and Ku₁₀₄ in the 7th period. It starts with Th₉₀ to Lr₁₀₃ (14 elements) following Ac₈₉ which presents the similarities with them. For this reason they are called Actinides.

Since the last electron in the atoms of these elements enters f subshell belonging to anti-penultimate shell, meaning (n-2)th shell, these elements are called f-Block Elements. The general form of their electronic configuration can be presented as (n-2) f⁰⁻¹⁴. (n-1) d⁰⁻². ns².

Lanthanides: 4 f-block elements

Lanthanides are present in 6th period of periodic table and the last electrons in these elements enter to (6-2) f sub-shell. Thus lanthanides are also called 4 f-Block Elements. There are hence defined as those elements in which the last electron goes to 4f sub-shell.

General properties of lanthanides and their trends

Electronic configuration: The general form of electronic configuration of Lanthanides is [Xe]₅₄ 4f²⁻¹⁴ 5d⁰⁻¹ 6s². These elements' configurations have 6s² in common but present variable occupancy of 4f level and 5d orbitals should remain singly-filled. Since the energy of 5d and 4f orbitals is closely similar in all lanthanides excepting Gd₆₄ (Gadolinium) and Lu₇₁ (Lutetium), 5d¹ electron get shifted to 4f and hence 5d remain vacant. In Gd₆₄ a shifting of 5d¹ electron to 4f doesn't take place because it gives an unstable configuration. In Lu₇₁ a shifting of 5d¹ electron to 4f is not possible because 4f is already filled to their maximum capacity of 14 electrons.

Oxidation state: The main oxidation state of lanthanide is +3. Although a few lanthanides also show +2 and +4 oxidation states, +3 is a most stable oxidation state for all lanthanides since some M⁺² and M⁺⁴ ions are converted into M⁺³ ions. Example: Sm⁺² is a good reducing agents while Ce⁺⁴ is a good oxidizing agent since both these ions are converted into M⁺³ ions which are most stable ions.

Atomic and ionic radii: Atomic and ionic radii decrease from left to right as atomic number increases. The steady decrease in atomic and ionic radii of (M⁺³ ions) of lanthanide elements with increasing atomic number is called lanthanide contraction.

Cause of lanthanide contraction: as we precede from one element to the next in lanthanide series the nuclear charge (atomic number) increases by +1 at each next element. Thus as we move from La₅₇ to Lu₇₁ the attraction between the nucleus and outer most shell electron increases gradually in each step. It is also known that from La₅₁ to Lu₇₁ the addition of extra electron take place to 4f orbitals.

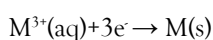
Since 4f have very diffused shape, the electrons in these orbitals are not able to shield effectively the attraction of nucleus for the electron in the outer most shell as the atomic number increases. It means that due to poor shielding of 4f and gradual increase of nuclear charge that lanthanide contractions take place among lanthanides.

Consequences of lanthanide contraction

Covalent character: As a result in decrease in size the covalent character between M^{3+} ions and OH ions increases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. It means that covalent character increase as atomic number increase, therefore $\text{Lu}(\text{OH})_3$ is most covalent whereas $\text{La}(\text{OH})_3$ is least covalent.

Table 2: The values of reduction potentials increase from La to Lu, values become less negative as we move from La to Lu.

Elements	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Eo in volt	-2.52	-2.48	-2.46	-2.43	-2.42	-2.41	-2.4	-2.39	-2.39	-2.35	-2.32	-2.3	-2.28	-2.27	-2.25



Those values of reduction potentials explain the below properties.

Reducing power: Lanthanides have high negative E^0 values, these elements have strong tendency to lose their electron to undergo oxidation hence are strong reducing agents. From La_{57} to Lu_{71} reduction potential increase, hence reducing power of these elements decrease from La_{57} to Lu_{71} .

Oxidizing power: As we move from left to right (from La to Lu) reduction potential increases electron tend to gain electron to undergo reduction hence are strong oxidizing agents, from La to Lu oxidizing capacity increase.

Electropositive character: Due to negative E^0 values lanthanide readily lose their electron and hence strong electron positive (metallic character) metallic character decrease from La to Lu as reduction potential increase.

Actinides: 5 F-block elements

Actinides are present in 7th of the periodic table the last electrons in these elements goes (7-2)f or 5f sub shell. Thus actinides are called 5f-block element. Actinides are those elements in which the last electron enters 5f subshell.

General properties of actinides and their trends

Electronic configuration: The general electronic configuration of actinides is $5f^{0-14}.6d^{0,2}.7s^2$. As we move in the series of actinides the additional of electron should occupy the vacant 5f while 6d orbital should be remain singly-filled. The expected configurations of actinide atoms should be those in which 6d is singly-filled and 5f orbitals are progressively filled up with electron means that expected configuration should be $[\text{Rn}]_{86} 5f^{1-14} 6d^1 7s^2$ but since the energies of 6d and 5f are the same, in Th_{90} 5f¹ electron get shifted to 6d orbital. On the other hand in all other elements 6d¹ electron shift to 5f orbitals except Cm_{96} in which the shifting of 6d¹ electron doesn't take place because this shifting gives unstable electronic configuration, and in Lr_{103} which has 5f already having 14 electrons.

Atomic radius and ionic radii: Important oxidation states exhibited by actinides are: +2, +3,+4,+5,+6 and +7. Oxidation state +3 is shown by all the actinides and it becomes a more and more stable as the atomic number increases across the period.

Basic character of lanthanide hydroxide, $M(\text{OH})_3$: Due to lanthanide contraction the size M^{3+} Lanthanide ions decreases regularly with increase of atomic number as result in decrease in size basic character of the hydroxide decreases with increase in atomic number. Consequently $\text{La}(\text{OH})_3$ is most basic while $\text{Lu}(\text{OH})_3$ is least basic.

Similarities among lanthanides: Because very small change in radii of lanthanide their chemical properties are quite similar. It cannot be separated from each other in pure state.

Properties depend on reduction potential: The values of reduction potentials (E^0 values) for reduction reaction (Table 2):

CONCLUSION

Considering the ionic radii of M^{3+} and M^{4+} actinide ions the general observation shows that there is a steady decrease in the size of M^{3+} and M^{4+} cations and this is called actinide contraction. As discussed in the lanthanides series, the actinide contraction is caused by the increase in nuclear charge and the addition of extra electron which takes place in 5f orbital. As the shielding effect between the electrons in the same 5f orbital is very poor, the increase in nuclear charge by +1 at each next element in the actinide series brings the valence shell nearer to the nucleus and hence the size of M^{3+} and M^{4+} cations goes on decreasing as we move from one element to the next one in the series.

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