Lanthanide Contraction

Lanthanides are the rare earth elements of the modern periodic table, i.e. the elements with atomic numbers from 58 to 71, following the element Lanthanum.The atomic size or the ionic radii of tri positive lanthanide ions decrease steadily from La to Lu due to increasing nuclear charge and electrons entering the inner (n-2) f orbital. This gradual decrease in the size with an increasing atomic number is called lanthanoid contraction. Lanthanoid contraction is also known as lanthanide contraction Lanthanide contraction is the steady decrease in the size of the ions and atoms of the rare earth elements with increasing atomic numbers from lanthanum (atomic number 57) to lutetium (with an atomic number 71). For every consecutive atom, the nuclear charge can be more positive by a single unit, accompanied by the corresponding increase in the electron count present in the 4f orbitals surrounding the nucleus.

The 4f electrons imperfectly protect each other from the increased positive charge of the nucleus, resulting in a steady rise in the effective nuclear charge attracting every electron as the lanthanide elements progress, resulting in successive decreases in ionic and atomic radii.

Reason for lanthanoid contraction

1.Atomic size

2.Difficulty in the separation of lanthanides

3.Effect on the basic strength of hydroxides

4.Complex formation

5.The ionization energy of d-block elements.

Consequences of Lanthanide Contraction

The following points will depict the effect of lanthanide contraction more clearly:

- **Atomic Size**

  The size of the atom of the third transition series is approximately similar to that of the atom of the second transition series. For example, the radius of Zr = radius of Hf and the radius of Nb = radius of Ta, and so on.

- **Difficulty in the Separation of Lanthanides**

  As there is only a small change in the ionic radii of the Lanthanides, their chemical properties are the same. This makes the element's separation in the pure state difficult.

- **Effect on the Basic Strength of Hydroxides**

  As the size of the lanthanides decreases from the elements La to Lu, the covalent character of the hydroxides increases, and thus their basic strength decreases. Therefore, $Lu(OH)_3$ is said to be least basic, and La $(OH)_3$ is said to be more basic.

- **Complex Formation**

  Due to the smaller size, whereas, higher nuclear charge, the tendency to produce coordinate. Complexity increases from the element La^{3+} to Lu^{3+}.

- **Electronegativity**

  It increases from the elements La to Lu.

- **Ionization Energy**

Electron's attraction by the nuclear charge is higher, and thus Ionization energy of the 5d elements is much larger compared to 4d and 3d. In the 5d series, the total elements except Pt and Au contain a filled s-shell.

Elements from Hafnium to rhenium contain similar Ionization energy, and after that, the Ionization energy increases with the number of shared d-electrons such that Gold and Iridium hold the maximum Ionization Energy.

Cause of Lanthanide Contraction

The effect of lanthanide contraction results from the poor shielding of nuclear charge (with the attractive nuclear force on electrons) by 4f electrons; the 6s electrons can be drawn towards the nucleus, hence resulting in the smaller atomic radius.

In the case of single-electron atoms, the average separation of an electron from the nucleus is defined by the subshell it belongs to and decreases with an increased charge on the nucleus, where this, in turn, leads to the decrease in atomic radius. Whereas, in the case of multi-electron atoms, the decrease in the radius brought about by an increase in nuclear charge is partially offset by the increasing electrostatic repulsion among the electrons.

A "shielding effect" operates, in which existing electrons shield the outer electrons from the nuclear charge by causing them to undergo less effective charge on the nucleus as more electrons are applied to the outer shells. The inner electrons' shielding effect decreases in the following order: s > p > d > f.

In general, as a specific subshell is filled in a period, the atomic radius decreases. This particular effect is specifically pronounced in the case of lanthanides, as the 4f subshell that is filled across these elements is not more effective at shielding the outer shell (n=5 and n=6) electrons. Therefore, the shielding effect can be less able to counter the decrease in radius caused by an increasing nuclear charge. This leads to the "lanthanide contraction". And, the ionic radius drops from a range of 103 pm for lanthanum (III) to 86.1 pm for lutetium (III).

The relativistic effects have been blamed for up to 10% of the lanthanide contraction.