Unit – V

Chemistry of f-block elements

Lanthanide Series:

* Additional e^{-s} enters $(n-2)$ f orbitals are called inner transition elements
* f-block elements. because extra e^{-s} enter the f-orbital.
* Af block elements are also called Lanthanides or rare earths
* Ce – y is Lanthanide Series
* Similar physical & chemical properties

occurance

(i) Cerium gp

* These are also called cerite – earth minerals or cerium earths and
* This gp contains largely elements of atomic numbers from 57-63.

ii) yttrium gp minerals:

* These are also called yttrium earth minerals (or) yttrium earths.
* This gps contain 64 – 71

properties:

i) electronic configuration:

La $4f^0 5d^1 6s^2$

↓

Lu $4f^{24} 5d^0 6s^2$

ii) oxdn states:

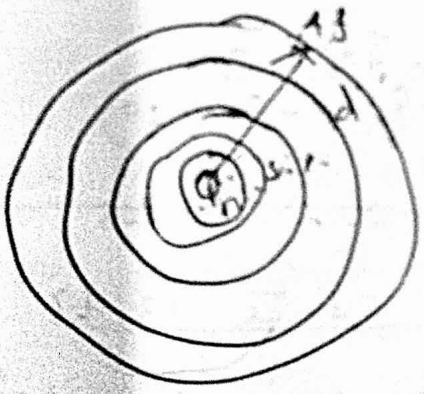
* tri positive (+3)
* half (or) completely filled orbital are more stable.
* formation of Ce^{4+}, La^{3+} ($4f^0$)
* ~~The Stability of order is +2 State~~
* ~~most Common State is +3~~
* The oxdn State is +2, +3, & +4
* most Common is +3

iii) Lanthanide contraction

* Decrease in the ionic radii of the elements from Lanthanum to Lutetium.
* The term was coined by the Norwegian geochemist

Effects:

* The increased attraction of the outer shell e^{-s} across the Lanthanide period.
* Decrease in ionic radii from La^{3+} — Lu^{3+}
* Across the Lanthanide series e^{-s} are added to the 4f-shell.
* The first f shell is inside the full 5S & 5P Shells,



* Decrease the ionic radii doesn't affect chemical

* without Lanthanide contraction, a chemical Separation of Lanthanide Contraction, a chemical Separation of ~~Period~~ Lanthanides would be extremely difficult.

* Lutetium is hardest densest.

* Lanthanide has the highest m.p.

Causes:

* Size will be decrease and resulting in a smaller atomic radius.

* Decreases with increasing charge on the nucleus.

* Decreases the atomic radii.

* increasing electrostatic repulsion among the e^{-s}

* e^{-s} added in outer shells e^{-s} already present in shield the outer e^{-s} from nuclear charge.

* The shielding effect exerted by the inner e^{-s} decreases in the order

$$s > p > d > f$$

(iv) Magnetic Properties:

* paramagnetic behaviour shows unpaired e^{-s}
* La^{3+} & Lu^{3+} did not contain unpaired e^-
* other +3 ions are paramagnetic
* e^{-s} motion (or) orbital motion are possible in this gp elements
* Paramagnetic value do not depending on the no. of unpaired e^{-s} only.
* Af e^{-s} are responsible for the strong magnetic nature.
* At high. temp. all Lanthanides except Lu. are paramagnetic
* At low temp. many metals exihibit antiferromagnetism.
* Very low temp. no. of elements becomes ferromagnetism

* Paramagnetism depends only e^- moments

(i) diamagnetic nature:

* $\mu < 1$
* The compd in magnetic field magnetic magnetic lines are not allow this compds.

$$\chi = \frac{\mu - 1}{4\pi\rho}$$

μ = -ve
ρ - magnetic permeability
μ - magnetic susceptibility

(ii) Paramagnetic nature:

* $\mu > 1$
* Compds in magnetic field, magnetic lines are goes to this compds contain no empty place.

$$\chi = \frac{\mu - 1}{4\pi\rho}$$

(iii) Ferromagnetic nature:

* 1000 times greater magnetic susceptibility.

(eg) Fe, Co, Ni

* Increases the temp. decreases the magnetic permiability called Curie point or Curie temp.

(IV) Antiferromagnetism: nature

* Magnetic values are low and +ve in particular temp called Neel point (or) neel temp.

(V) Complex formation:

* highly electropositive
* big size (0.85 – 1.03Å°). So should not give complex.
* Should form Complex with π-bond ligands.
* f-orbital should not involved π-bonds
* But gives Complex with EDTA, oxalic acid, Ethylene diamine called Chelate ligands.

Actinides:

* first element is Actinium.
* 5f - block elements
* increases atomic no: decreases the size.
* f-orbital having no screening effect.
* Actinide Contraction is same as Lanthanide contraction.
* Actinium — Lawrencium => 14 elements are called actinides.

Properties:

* +2, +3, +4, +5, +6 oxdn is common.
* Th & U are diamagnetic
* most elements have +4 oxdn state. Some elements +5, +6 states are occurs.
* Actinides gives halide complexes
  eg $K[ThCl_5]$, $K_2[ThCl_4]$
* $ThCl_4$ with KCl at RB gives $ThCl_4$, $ThBr_4$

Actinide contraction:

* increases atomic no: decreases the size.