

LANTHANOIDS AND ACTINOIDS

(Chemistry-DSE-1002D: Inorganic and Physical Chemistry, Section-I)

BY

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OBJECTIVES

A] Lanthanoids

1. Introduction
2. electronic configurations
3. oxidation states
4. colour and spectra
5. magnetic properties
6. lanthanide contraction
7. occurrence and separation of lanthanides (ion exchange method).

B] Actinoids

1. Introduction
 2. position in periodic table
 3. electronic configuration
 4. oxidation states
 5. General methods of preparation of Transuranic elements-
 - i) Neutron capture followed by β decay
 - ii) Accelerated projectile bombardment
 - iii) Heavy ion bombardment
 6. IUPAC nomenclature of the super heavy elements with atomic number (Z) greater than 100.
- 

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d-block: transition elements

Period	1A (1)	2A (2)	TRANSITION ELEMENTS d-block										3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
			3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	(9)	(10)	1B (11)	2B (12)						
1																		
2																		
3																		
4			21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn						
5			39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd						
6			57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg						
7			89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112						

INNER TRANSITION ELEMENTS
f block

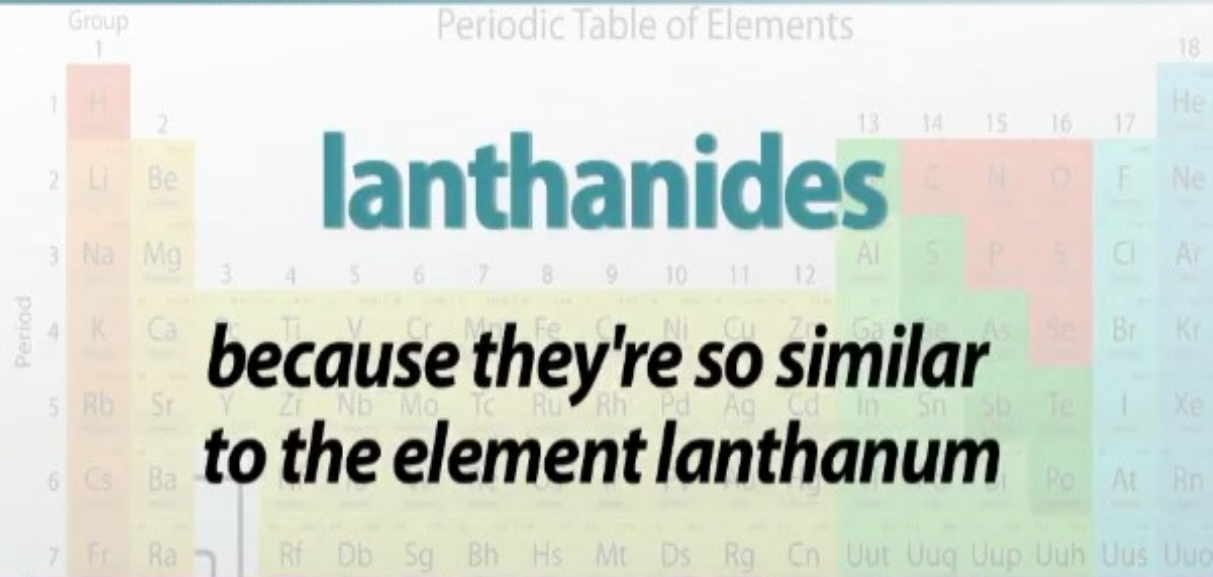
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

f-block:
inner transition elements



LANTHANIDE SERIES ELEMENTS

Periodic Table of Elements



57	138.90	58	140.16	59	140.90	60	144.24	61	(145)	62	150.36	63	151.96	64	157.25	65	158.92	66	162.50	67	164.93	68	167.25	69	168.93	70	173.05	71	174.96
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu															
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium															



INNER TRANSITION ELEMENTS

The elements in which the additional electrons 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	Symbol	Atomic Number	Expected electronic configuration	Observed electronic configuration
Lanthanum	La	57	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe] 4f ⁰ 5d ¹ 6s ²
Cerium	Ce	58	[Xe] 4f ¹ 5d ¹ 6s ²	[Xe] 4f ² 5d ⁰ 6s ²
Praseodymium	Pr	59	[Xe] 4f ² 5d ¹ 6s ²	[Xe] 4f ³ 5d ⁰ 6s ²
Neodymium	Nd	60	[Xe] 4f ³ 5d ¹ 6s ²	[Xe] 4f ⁴ 5d ⁰ 6s ²
Promethium	Pm	61	[Xe] 4f ⁴ 5d ¹ 6s ²	[Xe] 4f ⁵ 5d ⁰ 6s ²
Samarium	Sm	62	[Xe] 4f ⁵ 5d ¹ 6s ²	[Xe] 4f ⁶ 5d ⁰ 6s ²
Europium	Eu	63	[Xe] 4f ⁶ 5d ¹ 6s ²	[Xe] 4f ⁷ 5d ⁰ 6s ²
Gadolinium	Gd	64	[Xe] 4f ⁷ 5d ¹ 6s ²	[Xe] 4f ⁷ 5d ¹ 6s ²
Terbium	Tb	65	[Xe] 4f ⁸ 5d ¹ 6s ²	[Xe] 4f ⁹ 5d ⁰ 6s ²
Dysprosium	Dy	66	[Xe] 4f ⁹ 5d ¹ 6s ²	[Xe] 4f ¹⁰ 5d ⁰ 6s ²
Holmium	Ho	67	[Xe] 4f ¹⁰ 5d ¹ 6s ²	[Xe] 4f ¹¹ 5d ⁰ 6s ²
Erbium	Er	68	[Xe] 4f ¹¹ 5d ¹ 6s ²	[Xe] 4f ¹² 5d ⁰ 6s ²
Thulium	Tm	69	[Xe] 4f ¹² 5d ¹ 6s ²	[Xe] 4f ¹³ 5d ⁰ 6s ²
Ytterbium	Yb	70	[Xe] 4f ¹³ 5d ¹ 6s ²	[Xe] 4f ¹⁴ 5d ⁰ 6s ²
Lutetium	Lu	71	[Xe] 4f ¹⁴ 5d ¹ 6s ²	[Xe] 4f ¹⁴ 5d ¹ 6s ²



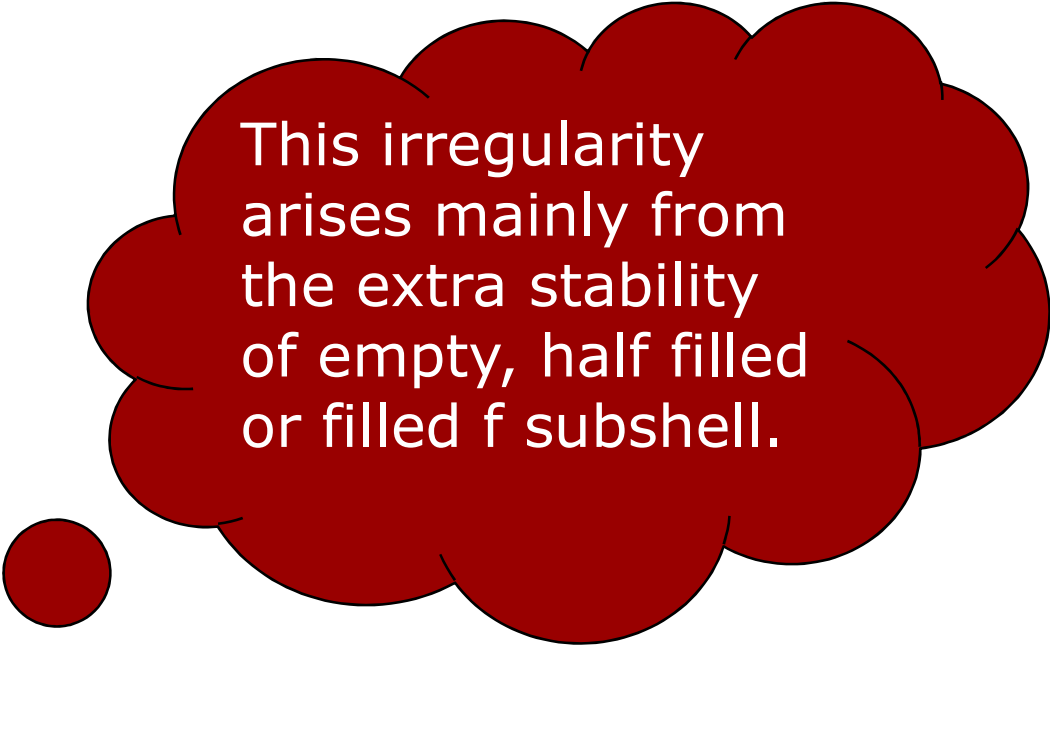
Some facts in electronic configuration of lanthanides

1. Three incomplete shells
2. Place between Ba (56) and Hf (72)
3. Addition of electrons in 4f sub-energy level
4. Similarities in properties
5. Anomalous behavior found in Gd and Lu




OXIDATION STATES

Predominantly +3 oxidation state.



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

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



Symbol	Idealized	Observed	M ³⁺	M ²⁺	M ⁺	At. Radii A*	N0. of f- electron
La	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe]	-		1.88	0
Ce	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ² 5d ⁰ 6s ²	4f ¹	4f ²	[Xe]	1.82	1
Pr	[Xe]4f ² 5d ¹ 6s ²	[Xe]4f ³ 5d ⁰ 6s ²	4f ²	-	4f ¹	1.83	2
Nd	[Xe]4f ³ 5d ¹ 6s ²	[Xe]4f ⁴ 6s ²	4f ³	4f ⁴	4f ²	1.82	3
Pm	[Xe]4f ⁴ 5d ¹ 6s ²	[Xe]4f ⁵ 6s ²	4f ⁴	-	-		4
Sm	[Xe]4f ⁵ 5d ¹ 6s ²	[Xe]4f ⁶ 6s ²	4f ⁵	4f ⁶	-	1.80	5
Eu	[Xe]4f ⁶ 5d ¹ 6s ²	[Xe]4f ⁷ 6s ²	4f ⁶	4f ⁷	-	2.04	6
Gd	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷ 5d ¹ 6s ²	4f ⁷	-	-	1.80	7
Tb	[Xe]4f ⁸ 5d ¹ 6s ²	[Xe]4f ⁹ 6s ²	4f ⁸	-	4f ⁷	1.78	8
Dy	[Xe]4f ⁹ 5d ¹ 6s ²	[Xe]4f ¹⁰ 6s ²	4f ⁹	-	4f ⁸	1.77	9
Ho	[Xe]4f ¹⁰ 5d ¹ 6s ²	[Xe]4f ¹¹ 6s ²	4f ¹⁰	-	-	1.77	10
Er	[Xe]4f ¹¹ 5d ¹ 6s ²	[Xe]4f ¹² 6s ²	4f ¹¹	-	-	1.76	11
Tm	[Xe]4f ¹² 5d ¹ 6s ²	[Xe]4f ¹³ 6s ²	4f ¹²	4f ¹³	-	1.75	12
Yb	[Xe]4f ¹³ 5d ¹ 6s ²	[Xe]4f ¹⁴ 6s ²	4f ¹³	4f ¹⁴	-	1.94	13
Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴	-	-	1.73	14

➤ The configuration of La^{3+} ion, is that of xenon which is highly stable. So, it is not possible to have a La^{+4} ion.

➤ In the same way Ga, Lu also form only +3 ions, because the removal of three electrons give stable half filled $4f^7$ configuration for Gd^{3+} ion and in completely filled $4f^{14}$ configuration for Lu^{3+} ions.

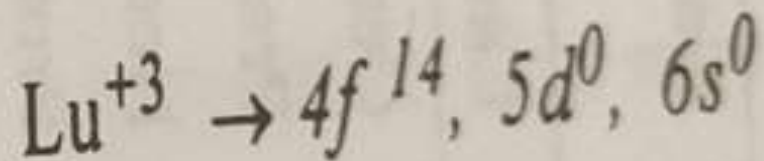
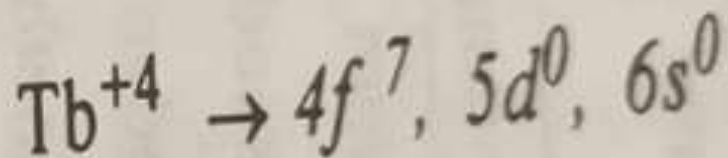
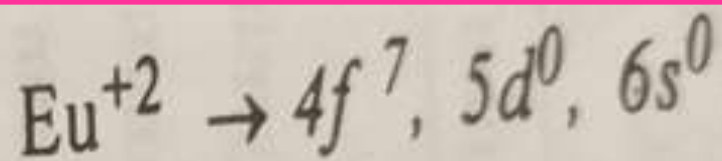
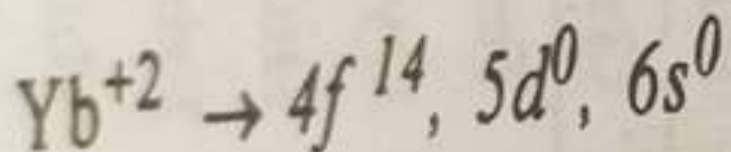
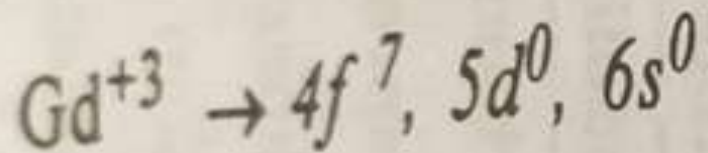
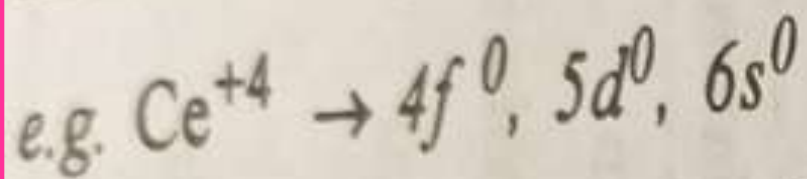
➤ In other Lanthanides, +2 and +4 oxidation states also occur but these are always **less stable than the +3 oxidation** state which is characteristic of this family

➤ The +2 and +4 oxidation states are shown by those elements which will attain **f^0 , f^7 and f^{14}** configurations by doing so

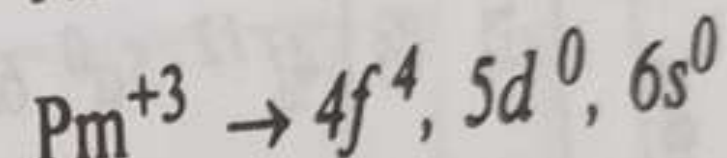
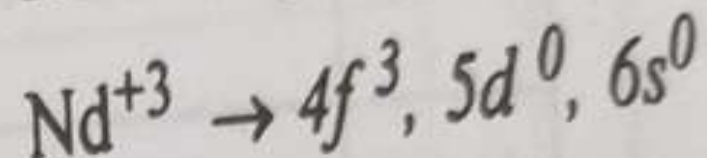
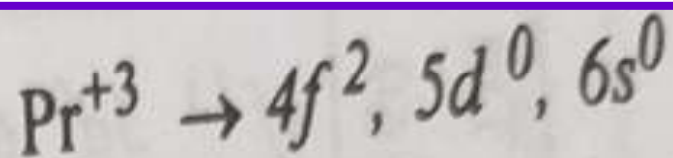
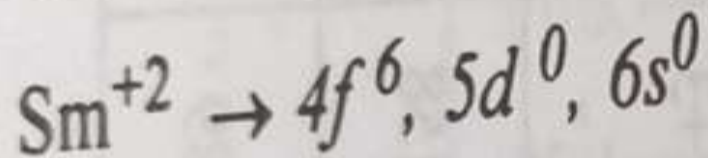
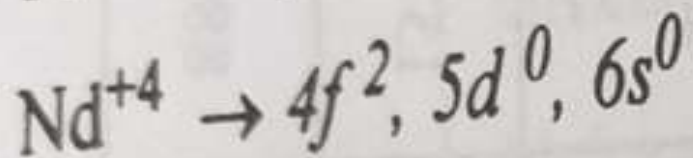
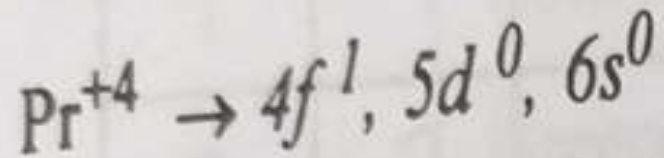
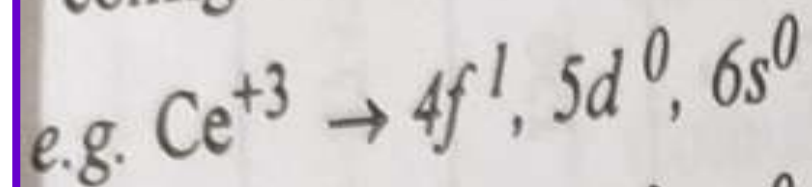
➤ For eg. Ce^{4+} , Eu^{2+} are $4f^7$, Tb^{4+} - $4f^7$, Yb^{2+} - $4f^{14}$

extra stability is associated with f^0 , f^7 , f^{14} configurations.

filled and completely filled



4 configurations.



COLOUR OF LANTHANIDES

- The colour of the lanthanides emerge from f to f transitions .
- $f \rightarrow f$ transitions are much weaker and narrower than those from $d \rightarrow d$ transitions
- This makes the colours of lanthanide complexes far fainter than those of transition metal complexes.

- The colour arises due to electronic transition within the 4f level (f – f transition)

- Absorption bands are extremely sharp line-like bands and these bands become more narrow as the temperature is lowered

4f orbitals lie deep in the atoms and are effectively shielded from the surroundings by the overlying 5s and 5p orbitals. Consequently, the absorption bands arise mainly from the electronic transitions within the 4f levels

- Thus the absorption bands show little dependence on the nature of the ligands

- f-d transitions are allowed transitions and result in intense absorption bands

- Lanthanides are silvery white but many lanthanide ions are coloured
- The colours remain same even on the change of anions

Sm₂O₃ and SmCl₃·6H₂O both are yellow in colour

- The colour of the ions depends upon the number of unpaired electrons.

La³⁺ (0) → colourless, Lu³⁺ (14) → colourless

- Ions containing *n*f electrons have almost similar colour to those with (14 – *n*) f electrons.

Eu³⁺ (6) → pale pink ← (8) Tb³⁺

- Some di and tetra positive ions having same number of electrons as tripositive ions do not have same colour.

Sm²⁺ (Blood red) → 6 ← Eu³⁺ (pale pink)

Table 2.3 : Colour of the Ln^{3+} ions

Ions	$n = \text{No. of } 4f \text{ electrons}$	Colour	n and x
La^{3+}	0	Colourless	0
Ce^{3+}	1	Colourless	1
Pr^{3+}	2	Green	2
Nd^{3+}	3	Pink	3
Pm^{3+}	4	Pink yellow	4
Sm^{3+}	5	Yellow	5
Eu^{3+}	6	Pale pink	6
Gd^{3+}	7	Colourless	7
Tb^{3+}	8	Pale pink	(x) 6
Dy^{3+}	9	Yellow	5
Ho^{3+}	10	Pink yellow	4
Er^{3+}	11	Pink	3
Tm^{3+}	12	Green	2
Yb^{3+}	13	Colourless	1
Lu^{3+}	14	Colourless	0

$x = 14 - n$

Magnetic Behaviour

❖ La⁺³ and Lu⁺³ do not contain any unpaired electrons, so they do not show paramagnetism. **All other tri positive ions of lanthanides are paramagnetic.**

❖ the 4f electrons are **deep inside** the ion and are well shielded from the quenching effect of the environment. The 4f-orbitals are **well shielded** from the surroundings by the overlying 5s and 5p-orbitals. As a result, the electric field of the ligands surrounding the ion **does not restrict the orbital motion of the electron**. So, in this case the observed paramagnetism is due to both factors – the electron spin and orbital motion.

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

S- spin contribution, L – Orbital contribution

❖ The magnetic moments of tri positive lanthanide ions are plotted against their respective atomic number. The value increases up to Nd⁺³ and then drops to (1.47) μ_B. It raises again and becomes maximum Dy⁺³ and starts dropping to zero for Lu⁺³ (f¹⁴) which is diamagnetic.

sulphates of M^{3+} ions ($n = \text{NO. of unpaired electrons}$)

M^{3+} ion	$4f^x$ electrons	n	Calculated value, $\mu_{cal} = g\sqrt{J(J+1)} \text{ BM}$ (Theoretical values)	Experimental value, μ_{exp} in (BM)
La^{3+}	$4f^0$ ($x = 0$)	0	0.00	Diamagnetic
Ce^{3+}	$4f^1$	1	2.54	2.3–2.5
Pr^{3+}	$4f^2$	2	3.58	3.4–3.6
Nd^{3+}	$4f^3$	3	3.62	3.5–3.6
Pm^{3+}	$4f^4$	4	2.70	—
Sm^{3+}	$4f^5$	5	0.84	1.5–1.6
Eu^{3+}	$4f^6$	6	0.00	3.4–3.6
Gd^{3+}	$4f^7$	7	7.94	7.8–8.0
Tb^{3+}	$4f^8$	6	9.70	9.4–9.6
Dy^{3+}	$4f^9$	5	10.65	10.4–10.5
Ho^{3+}	$4f^{10}$	4	10.60	10.3–10.5
Er^{3+}	$4f^{11}$	3	9.60	9.4–9.6
Tm^{3+}	$4f^{12}$	2	7.60	7.1–7.4
Yb^{3+}	$4f^{13}$	1	4.50	4.4–4.9
Lu^{3+}	$4f^{14}$ ($x = 14$)	0	0.00	Diamagnetic

The 4f electrons are responsible for the strong magnetism exhibited by the metals and compounds of the lanthanides. In the incomplete 4f subshell the magnetic effects of the different electrons do not cancel out each other as they do in a completed subshell, and this factor gives rise to the interesting magnetic behaviour of these elements.

At higher temperatures, all the lanthanides except lutetium are paramagnetic, and this paramagnetism frequently shows a strong anisotropy.

As the temperature is lowered, many of the metals exhibit a point below which they become antiferromagnetism (i.e., magnetic moments of the ions are aligned but some are opposed to others), and, as the temperatures are lowered still further, many of them go through a series of spin rearrangements, which may or may not be in conformity with the regular crystal lattice.

Finally, at still lower temperatures, a number of these elements become ferromagnetic (i.e., strongly magnetic, like iron). Some of the metals have saturation moments (magnetism observed when all the magnetic moments of the ions are aligned) greater than iron, cobalt, or nickel.

They also show a strong anisotropy in their magnetic behaviour depending on the crystal direction.



Paramagnetism. Magnetic properties have spin & orbit contributions (contrast "spin-only" of transition metals).

Magnetic moments of Ln³⁺ ions are generally well-described from the coupling of spin and orbital angular momenta - Russell-Saunders Coupling Scheme.

Spin orbit coupling constants are typically large (ca. 1000 cm⁻¹).

Ligand field effects are very small (ca. 100 cm⁻¹).

only ground J-state is populated.

spin-orbit coupling >> ligand field splittings.

magnetism is essentially independent of environment.

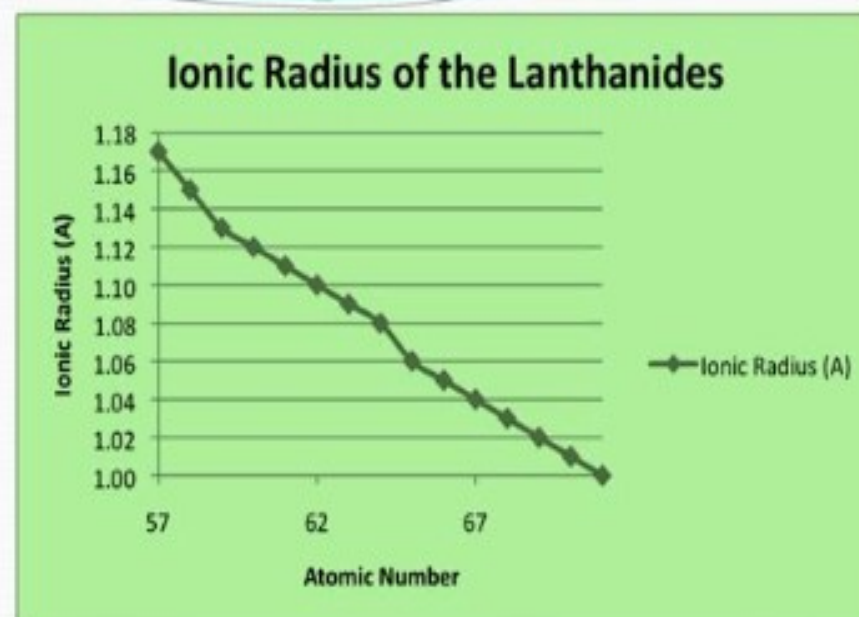
Magnetic moment of a J-state is expressed by the Landé formula:

$$\mu = g_J \sqrt{J(J+1)} \mu_B \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$



Lanthanide Contraction

Definition - The steady decrease in the size of the atoms and ions of the rare-earth elements with increasing atomic number from lanthanum (atomic number 57) through lutetium (atomic number 71) is known as the lanthanide contraction. For each consecutive atom the nuclear charge increases by one unit, accompanied by a corresponding increase in the number of electrons present in the 4f orbitals.



Cause – The new electrons enter the 4f orbital which have very poor shielding effect due to their diffused shape, as a result nuclear attraction increases and electron shells contract.

Consequences –

1. Among the lanthanides
2. Post Lanthanides

Consequences –



I Among Lanthanides –

1. **Basicity** of ions- decreases from La^{3+} to Lu^{3+} so their oxides and hydroxides are less basic
2. As the atomic size decreases across the series the elements following lanthanides show change in their physical properties.
 - a) The ionisation potential increases
 - b) Metallic nature decreases
 - c) Electropositivity decreases
 - d) Electronegativity Increases
 - e) Tendency to form complexes increases

II Post Lanthanides –

- i) **Occurrence of elements as pairs** – Due to similar size of 4d and 5d in a group, they have similar physical and chemical properties, they occur together in nature and their separation becomes very difficult.

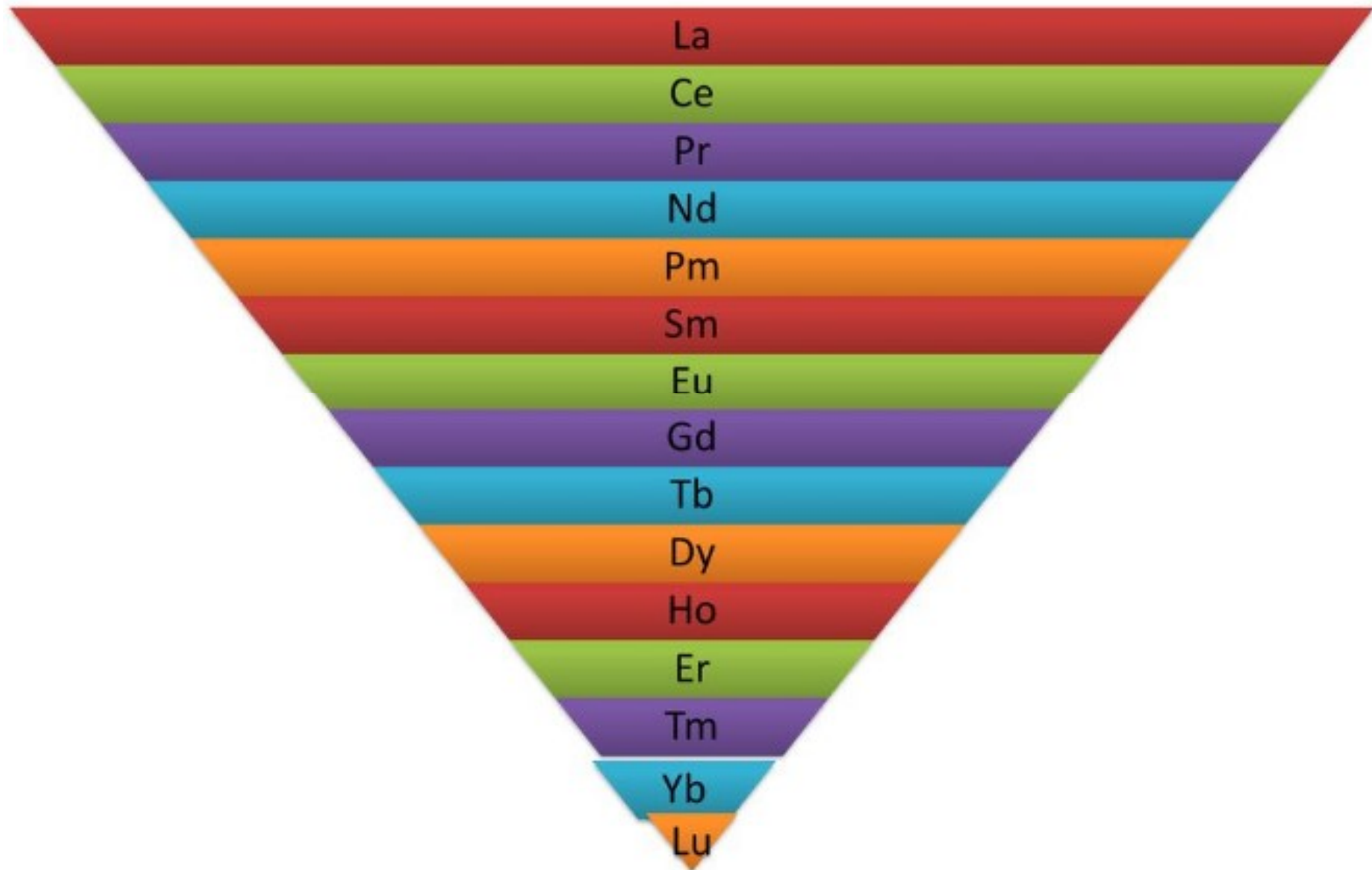
Zr/Hf, Nb/Ta, Mo/W

- ii) **Densities** – 5d elements have very high densities as down the group there is large increase in mass but no increase in volume.

III Occurrence of Yttrium along with heavier lanthanides –

yttrium has similar charge and size to Ho^{3+} & Er^{3+} hence it occurs with and separation is difficult.

2) Separation of Lanthanides:-



Separation of Lanthanides

- **Fractional crystallisation method**

The separation of lanthanide ions by this method is based on the slight differences in solubility.

- **Fractional precipitation method**

The differences in stability of lanthanide complexes is the basic principle of this method

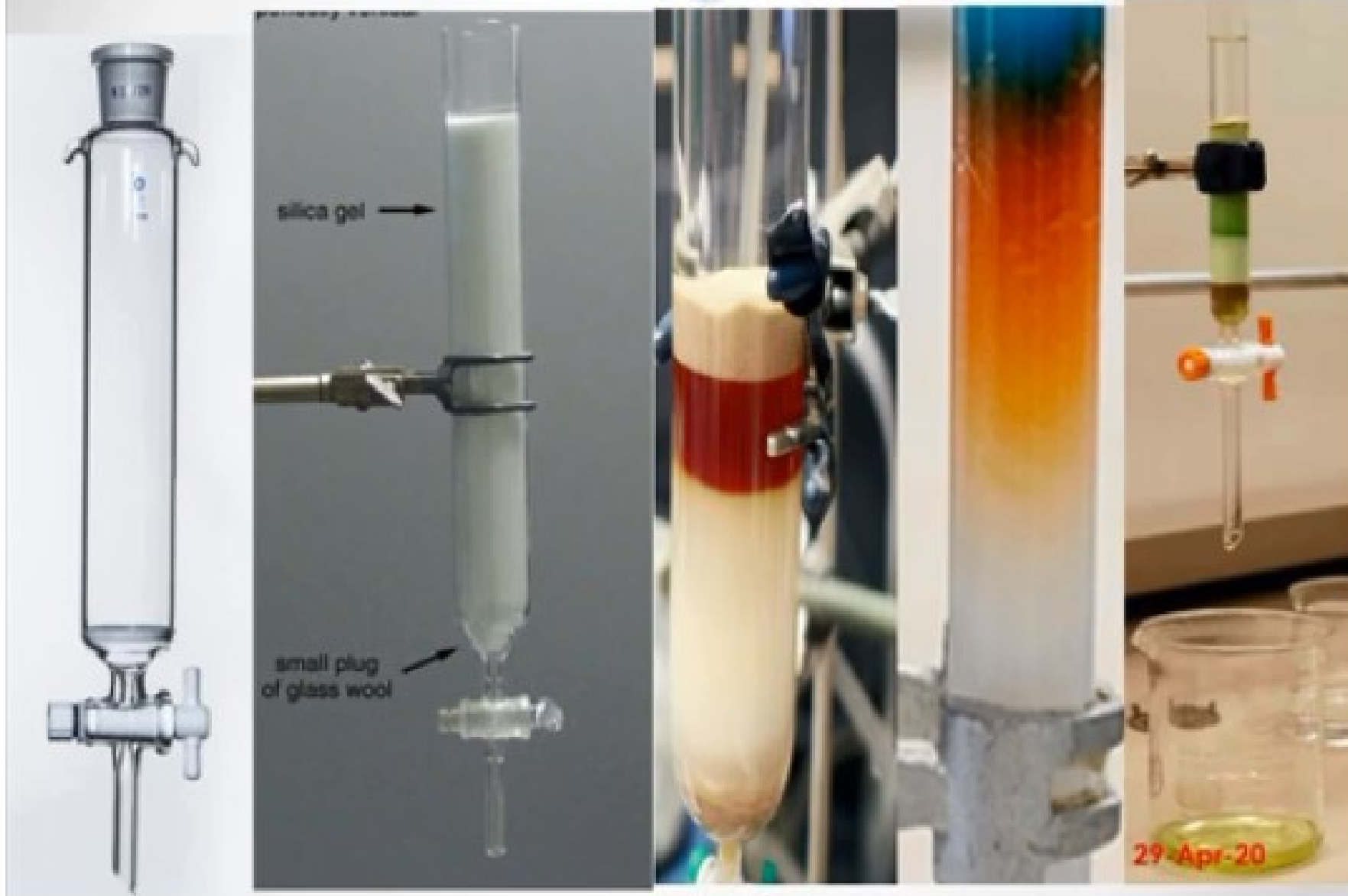
- **Solvent extraction method**

This method works on the slight difference in the partition coefficients of the salts of lanthanides between water and an organic solvent.

- **Ion exchange method**

This is the most elegant for lanthanide separation. It is based on the principle of selective exchange of lanthanide ions with the H_+ ion of a cation exchange resin.

Ion-Exchange method



ION EXCHANGE CHROMATOGRAPHY

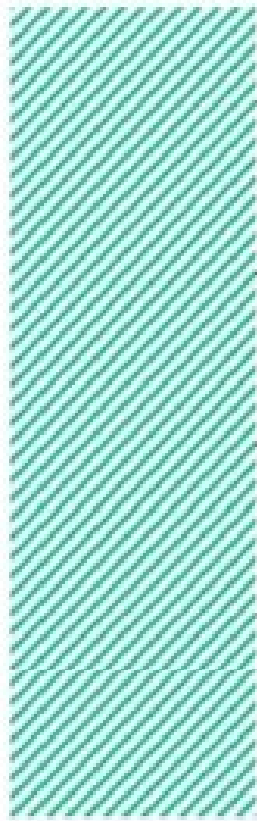
H⁺

**Stationary
Phase (Solid)
Ion exchange Resin**

**Mobile phase
Liquid**

Ion Exchange

Ion exchange is an adsorption phenomenon where the mechanism of adsorption is electrostatic. Electrostatic forces hold ions to charged functional groups on the surface of the ion exchange resin. The adsorbed ions replace ions that are on the resin surface on a 1:1 charge basis. For example:



$R^- - H^+$

$R^- - H^+$

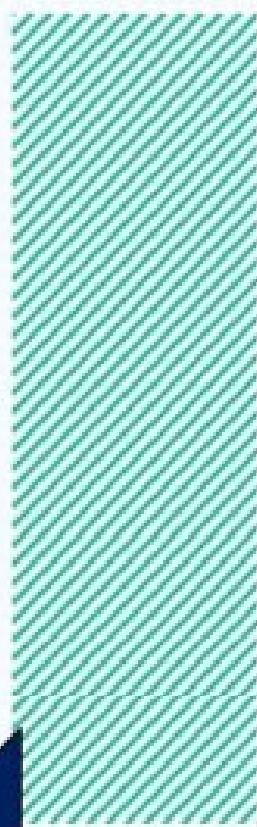
$R^- - H^+$

$R^- - H^+$



H^+

$+ 4 Na^+ \rightarrow$



$R^- - Na^+$

$R^- - Na^+$

$R^- - Na^+$

$R^- - Na^+$



Na^+



What are ion exchange resins ?

Polymeric resins are made in 3-D networks by cross-linking hydrocarbon chains. The resulting resin is insoluble, inert and relatively rigid. Ionic functional groups are attached to this framework

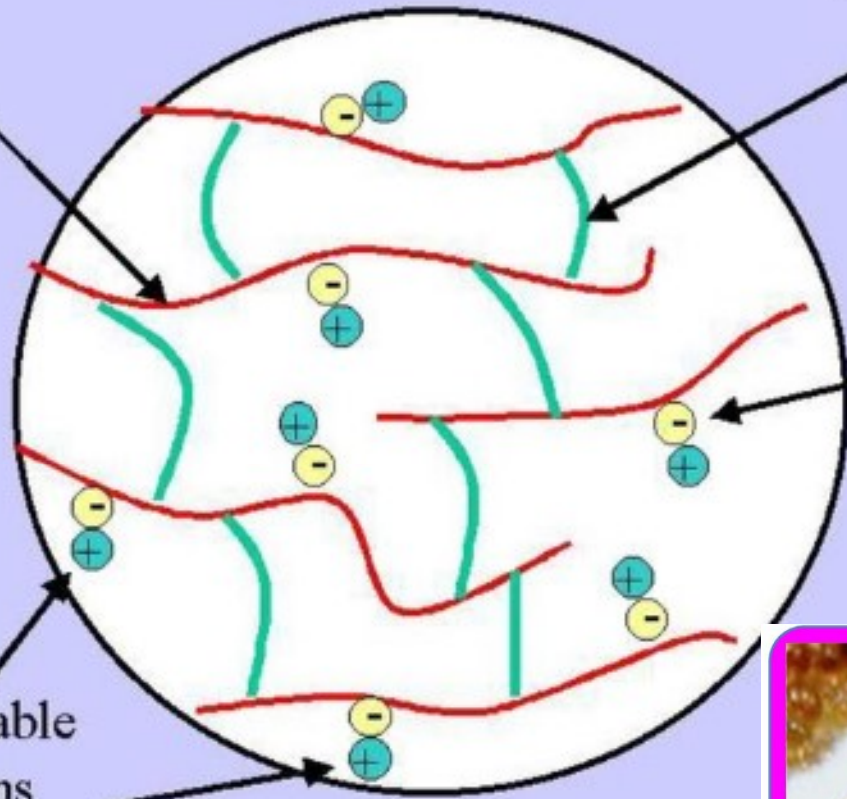
Polymer chains

Cross-links

INTEGRAL PART

Fixed resin functional groups

Exchangeable Counterions



Ion exchange resins

**CHARACTERISTICS
OF
ION EXCHANGE
RESINS**

```
graph LR; A[CHARACTERISTICS OF ION EXCHANGE RESINS] --- B[It should be insoluble in aqueous medium.]; A --- C[Should be denser than water]; A --- D[Should have loose porous polymeric structure.]; A --- E[It should be inert in nature]; A --- F[Should have large exchangeable sites]; A --- G[Should have high degree of cross linking.];
```

It should be insoluble in aqueous medium.

Should be denser than water

Should have loose porous polymeric structure.

It should be inert in nature

Should have large exchangeable sites

Should have high degree of cross linking.

TERMS INVOLVED

Elution

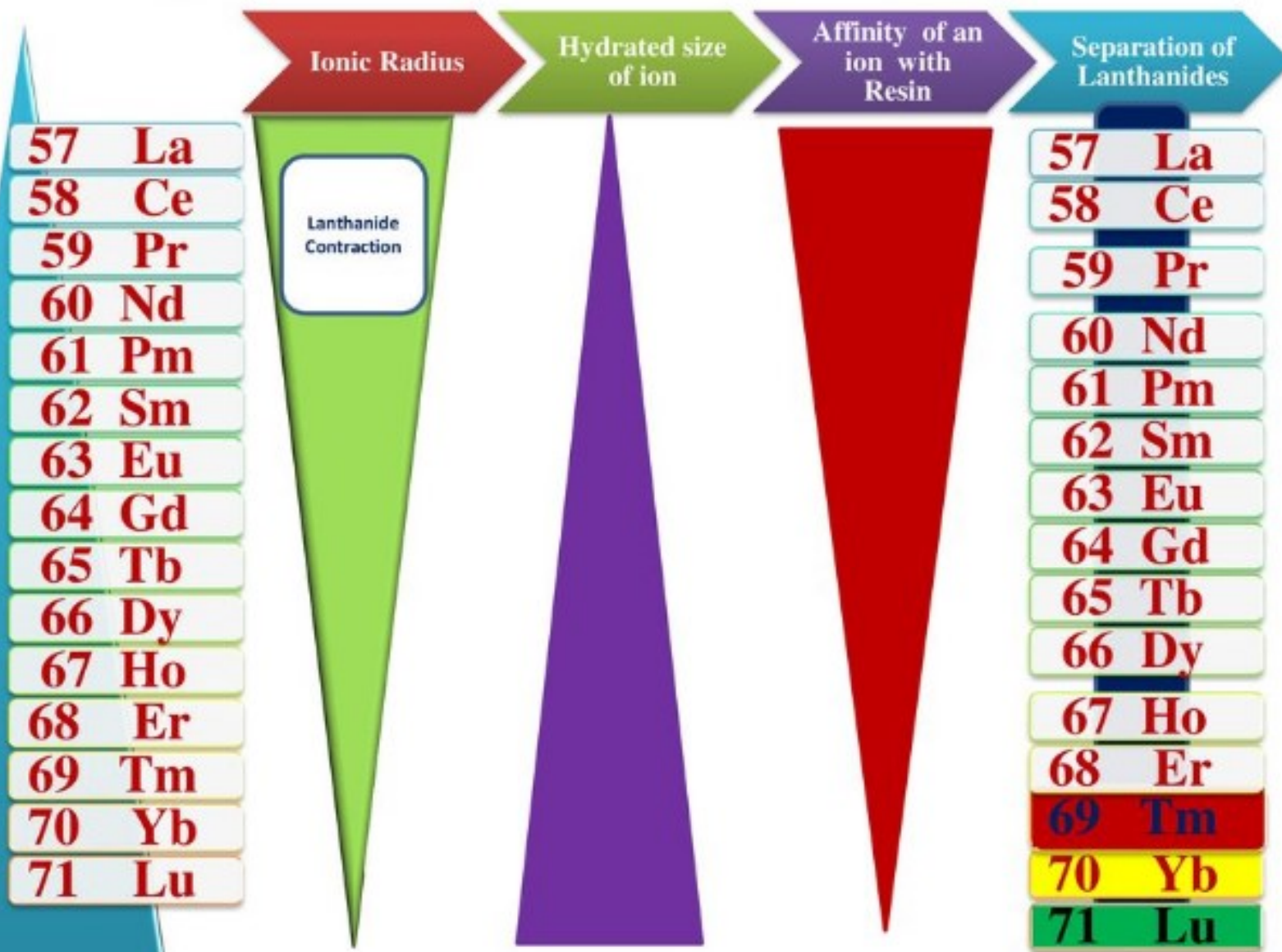
- The process of removing adsorbed ions is known as elution.

Eluent

- The solution used for elution is called as eluent .

Eluate

- The solution resulting from the elution is called as eluate.



In this column is packed with cation exchange resin of type R-H. When solution containing mixture of lanthanides is poured on the top of the then following equilibrium takes place,



In case of lanthanides the ionic radii of tripositive ions decreases with increase in atomic number i.e. from lanthanum to lutecium.

Hydration of ion increases with decrease in ionic size and therefore hydrated size of lanthanone ion increases with increase in atomic number.

Lanthanone ion having small hydrated size(La) will strongly adsorb on the resin and vice versa (Lu). Hence lanthanone ion held by resin decreases from La to Lu.

When HCL solution is passed as mobile phase separation of lanthanides takes place in reverse order of atomic number. Lutecium ion will separate out first where as Lanthanum ion separate at last.

For better separation elution is carried out using ammonium Citrate buffer at pH 2.8 -3.4.

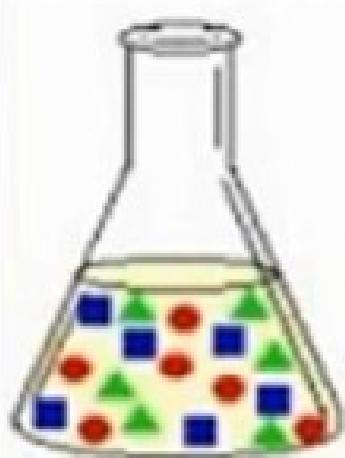
A synthetic **ion-exchange resin** with functional groups like $-\text{COOH}$ and $-\text{SO}_3\text{H}$ is packed in a long column fixed in a vertical position.

The steady decrease in size and consequent decrease in basicity causes the steady increase in the complexing ability with increasing atomic number of lanthanides. When an aqueous solution containing the mixture of trivalent lanthanide ion $\text{M}^{3+}(\text{aq})$ is passed through a column having synthetic cation-exchange resin $(\text{HR})_{\text{solid}}$, the **M^{3+} ions replace H^+ ion** of the resin and thus get fixed on that

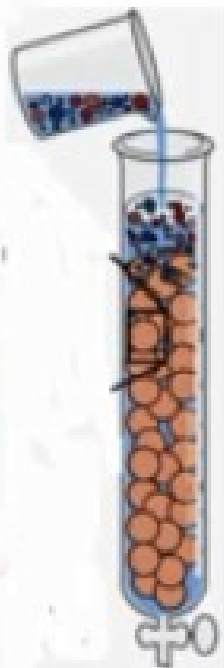


Ion-Exchange method

Lanthanide ion mixture (Ln^{3+}) passed through the glass column



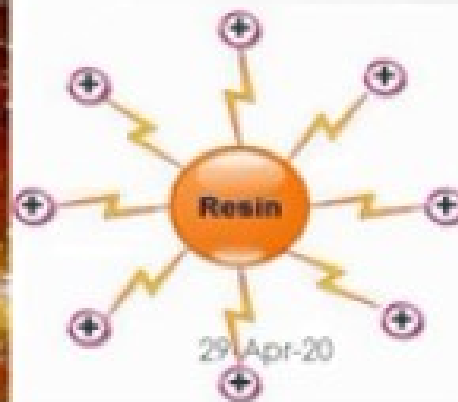
Mixture



Lanthanide ions are dissolved in water while the resin is solid.

Interaction between lanthanides and resin take place

Stationary phase - resin
Resin - Positive charge ion
to exchange

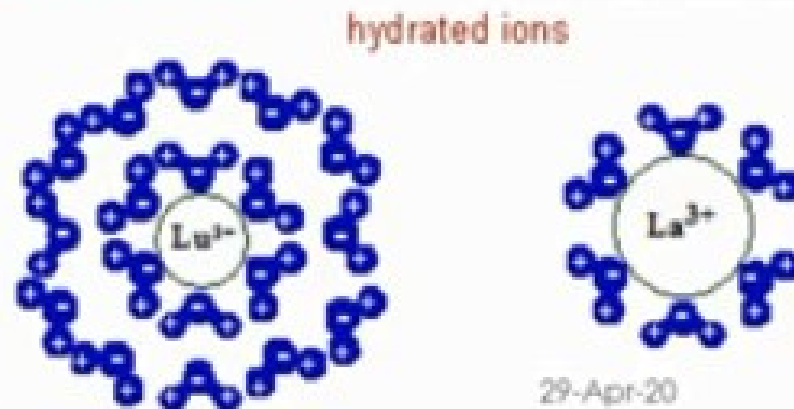


29 Apr-20

Ion-Exchange method

- Consider the following three lanthanide ions,
- La^{3+} , Gd^{3+} and Lu^{3+}
- Size variation,
- $\text{La}^{3+} > \text{Gd}^{3+} > \text{Lu}^{3+}$
- Lanthanum – large size, Lutetium – small size.
- Since the ions are **dissolved in water**, it is surrounded by water molecule. (**hydrated**)
- **Smaller the ion – greater the hydration.**

- Small hydrated ion-
strong binding with resin.
ie, held at the top of the
column

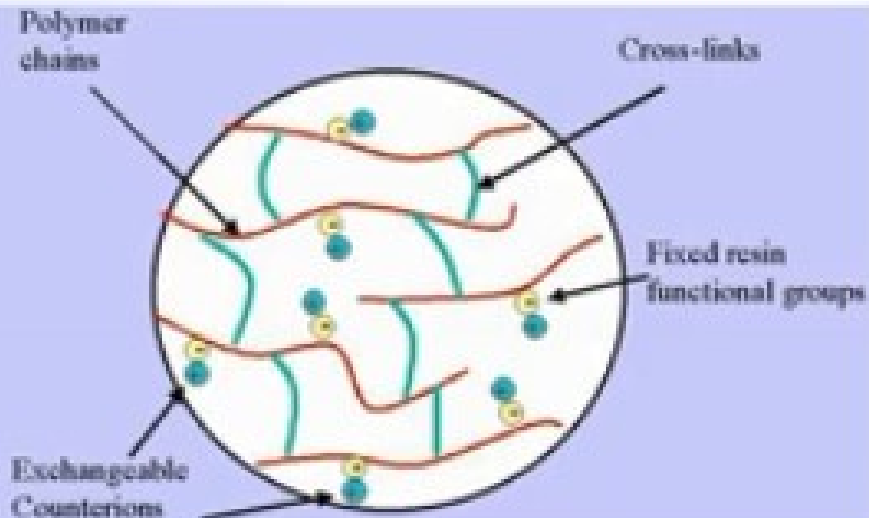


Ion-Exchange method

Eluent – *citric acid / ammonium citrate buffer.*



Lu^{3+} - comes first, La^{3+} - comes last

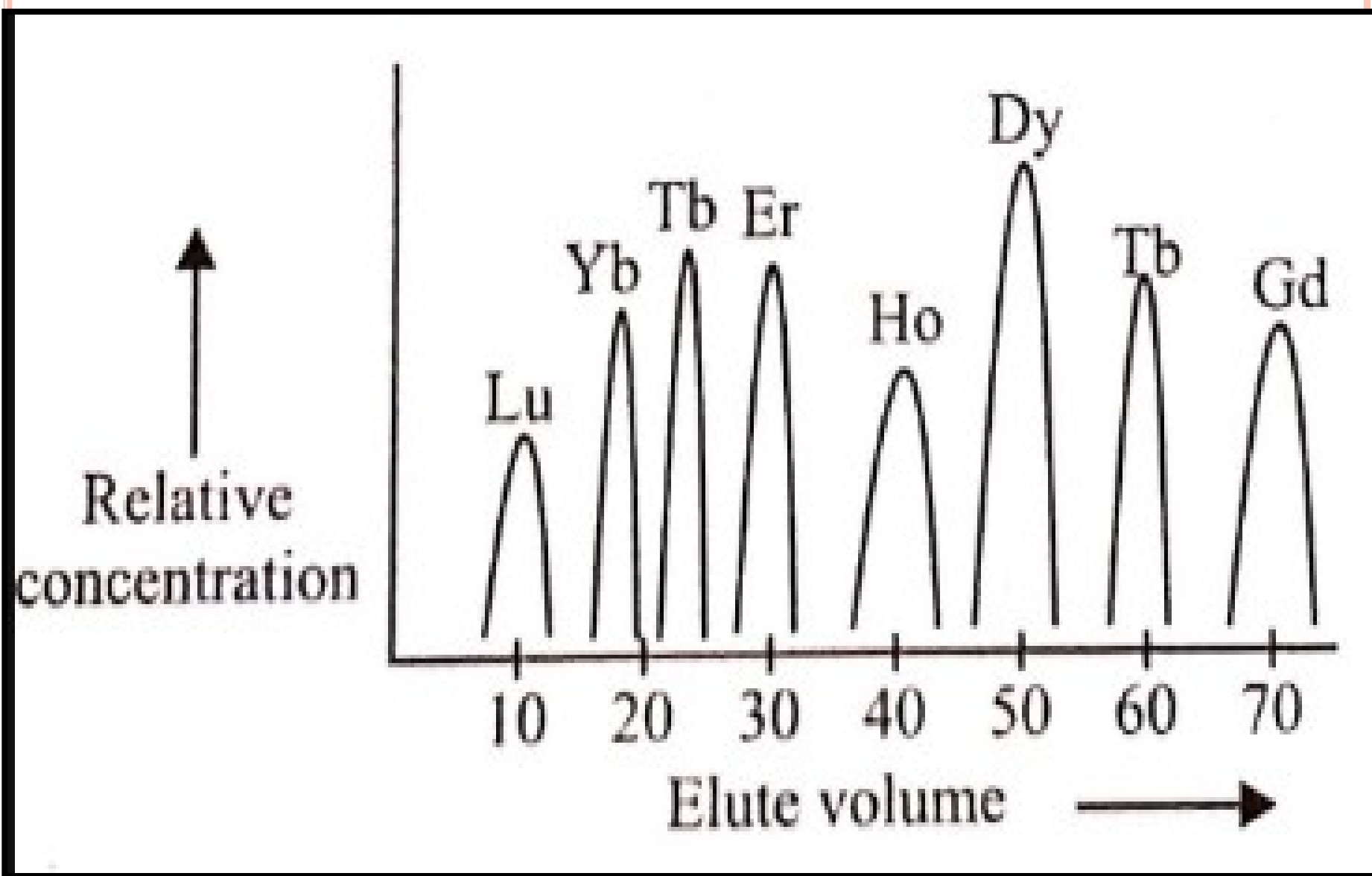


La^{3+}

Gd^{3+}

Lu^{3+}

29-Apr-20 •



Periodic Table of Elements

Group	1	2											13	14	15	16	17	18																																																									
Period 1	H																	He																																																									
Period 2	Li	Be											B	C	N	O	F	Ne																																																									
Period 3	Na	Mg											Al	S	P	S	Cl	Ar																																																									
Period 4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																																																									
Period 5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																																																									
Period 6	Cs	Ba											Tl	Pb	Bi	Po	At	Rn																																																									
<table border="1"> <tr> <td>Ac</td> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> <tr> <td colspan="3"></td> <td colspan="13"> <table border="1"> <tr> <td>La</td> <td>Ce</td> <td>Pr</td> <td>actinide series</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>Ac</td> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> </table> </td> </tr> </table>																			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				<table border="1"> <tr> <td>La</td> <td>Ce</td> <td>Pr</td> <td>actinide series</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>Ac</td> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> </table>													La	Ce	Pr	actinide series	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																																													
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INNER TRANSITION ELEMENTS

The elements in which the additional electrons 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.



3.4 : Position in Periodic Table

In the periodic table, actinides along with actinium are placed in one square of IIIB (3) group and seventh period. To give justice to every element, it should be allotted a separate square. They are placed at the bottom of the periodic table as a separate row. They are placed in one and the same square because

(i) If a separate square is given to each actinide, then the length of seventh period will be extended much more and will destroy the charm and symmetry of the periodic table. Hence, they are placed between $_{88}\text{Ra}$ and $_{104}\text{Rf}$.

(ii) All of them have common +3 oxidation state.

(iii) They are placed after francium and radium which belongs to *s*-block elements.

(iv) They may act as a bridge-between *s* and *d*-block elements.

Thus, the position of actinides in the periodic table is unchangable.

in BK 11

Table 3.1 : Names, symbols and electronic configurations of actinides.

Name	Symbol	Atomic number	Observed electronic configuration
Actinium	Ac	<u>89</u>	$[Rn] 5f^0 6d^1 7s^2$
Thorium *	Th	90	$[Rn] 5f^0 6d^2 7s^2$
Protactinium	Pa	91	$[Rn] 5f^2 6d^1 7s^2$
Uranium	U	92	$[Rn] 5f^3 6d^1 7s^2$
Neptunium	Np	93	$[Rn] 5f^4 6d^1 7s^2$
<u>Plutonium</u>	Pu	94	$[Rn] 5f^6 6d^0 7s^2$
Americium ↓	Am	95	$[Rn] 5f^7 6d^0 7s^2$
Curium	Cm	96	$[Rn] 5f^7 6d^1 7s^2$
Berkelium	Bk	97	$[Rn] 5f^9 6d^0 7s^2$
Californium	Cf	98	$[Rn] 5f^{10} 6d^0 7s^2$
Einsteinium	Es	99	$[Rn] 5f^{11} 6d^0 7s^2$
Fermium	Fm	100	$[Rn] 5f^{12} 6d^0 7s^2$
Mendelevium	Md	101	$[Rn] 5f^{13} 6d^0 7s^2$
Nobelium	No	102	$[Rn] 5f^{14} 6d^0 7s^2$
Lawrencium	Lr	<u>103</u>	$[Rn] 5f^{14} 6d^1 7s^2$

Electronic Configuration



Element	Seaborg view	Dawson View	Oxidation States
Ac	[Rd] 5f ⁰ 6d ¹ 7s ²	[Rd] 5f ⁰ 6d ¹ 7s ²	+3, +2
Th	[Rd] 5f ¹ 6d ¹ 7s ²	[Rd] 5f ⁰ 6d ² 7s ²	+4
Pa	[Rd] 5f ² 6d ¹ 7s ²	[Rd] 5f ⁰ 6d ³ 7s ²	+4, +5
U	[Rd] 5f ³ 6d ¹ 7s ²	[Rd] 5f ⁰ 6d ⁴ 7s ²	+4, +5, +6
Np	[Rd] 5f ⁴ 6d ¹ 7s ²	[Rd] 5f ⁴ 6d ¹ 7s ²	+4, +5, +6, +7
Pu	[Rd] 5f ⁵ 6d ¹ 7s ²	[Rd] 5f ⁵ 6d ¹ 7s ²	+4, +5, +6
Am	[Rd] 5f ⁶ 6d ¹ 7s ²	[Rd] 5f ⁶ 6d ¹ 7s ²	+3, +4, +5, +6
Cm	[Rd] 5f ⁷ 6d ¹ 7s ²	[Rd] 5f ⁷ 6d ¹ 7s ²	+3
Bk	[Rd] 5f ⁸ 6d ¹ 7s ²	[Rd] 5f ⁸ 6d ¹ 7s ²	+3
Cf	[Rd] 5f ⁹ 6d ¹ 7s ²	[Rd] 5f ⁹ 6d ¹ 7s ²	+3
Es	[Rd] 5f ¹⁰ 6d ¹ 7s ²	[Rd] 5f ¹⁰ 6d ¹ 7s ²	+3
Fm	[Rd] 5f ¹¹ 6d ¹ 7s ²	[Rd] 5f ¹¹ 6d ¹ 7s ²	+3
Md	[Rd] 5f ¹² 6d ¹ 7s ²	[Rd] 5f ¹² 6d ¹ 7s ²	+3
No	[Rd] 5f ¹³ 6d ¹ 7s ²	[Rd] 5f ¹³ 6d ¹ 7s ²	+2 (f ¹⁴)
Lr	[Rd] 5f ¹⁴ 6d ¹ 7s ²	[Rd] 5f ¹⁴ 6d ¹ 7s ²	+3

At No	Element	Symbol	Electron Configuration	M ³⁺ Radius A ⁰	M ⁴⁺ Radius A ⁰	Oxidation states	M P Oc
89	Actinium	Ac	[Rn] 5f ⁰ 6d ¹ 7s ²	1.11	---	3	817
90	Thorium	Th	[Rn] 5f ⁰ 6d ² 7s ²	(1.08)	0.94	(3) 4	1750
91	Protactinium	Pa	[Rn] 5f ² 6d ¹ 7s ²	1.04	0.90	(4) 5	1560
92	Uranium	U	[Rn] 5f ³ 6d ¹ 7s ²	1.03	0.87	(3,4,5) 6	1132
93	Neptunium	Np	[Rn] 5f ⁴ 6d ¹ 7s ²	1.01	0.86	(3,4,6) 5	639
94	Plutonium	Pu	[Rn] 5f ⁵ 6d ¹ 7s ²	1.00	0.85	(3,5,6) 4	640
95	Americium	Am	[Rn] 5f ⁶ 6d ¹ 7s ²	0.99	0.85	(4,5,6) 3	1170
96	Curium	Cm	[Rn] 5f ⁷ 6d ¹ 7s ²	0.98	0.83	(4) 3	1350
97	Berkelium	Bk	[Rn] 5f ⁸ 6d ¹ 7s ²	0.96	0.82	(4) 3	986
98	Californium	Cf	[Rn] 5f ¹⁰ 6d ⁰ 7s ²	0.95	---	3	(900)
99	Einsteinium	Es	[Rn] 5f ¹¹ 6d ⁰ 7s ²	---	---	3	(860)
100	Fermium	Fm	[Rn] 5f ¹² 6d ⁰ 7s ²	---		3	---
101	Mendelevium	Md	[Rn] 5f ¹³ 6d ⁰ 7s ²	---		3	---
102	Nobelium	No	[Rn] 5f ¹⁴ 6d ⁰ 7s ²	---		---	---
103	Lawrencium	Lw	[Rn] 5f ¹⁴ 6d ¹ 7s ²	---		---	---

General methods of preparation of Transuranic Elements

- ▶ Three general methods for preparation of transuranic elements
 - 1) Neutron bombardments
 - 2) Bombardment with accelerated particles or High voltage nuclei
 - 3) Heavy ion bombardments



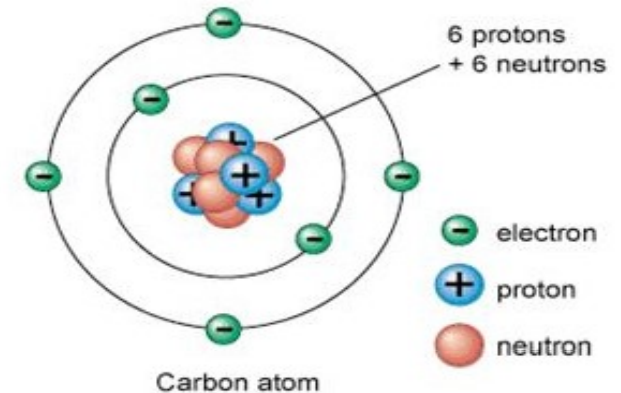
Comparison of Chemical and Nuclear Reactions:-

Chemical Reactions	Nuclear Reactions
One substance is converted into another, but atoms never change identity.	Atoms of one element typically are converted into atoms of another element.
Only Electrons take part in chemical reaction	Nucleus of element takes part in nuclear reaction.
Small amount energy evolved during chemical reaction	Large amount energy evolved during nuclear reaction
Reaction rates are influenced by temperature, concentration and catalyst.	Reaction rates are depend on concentration of element, but not influenced by temperature, catalyst.

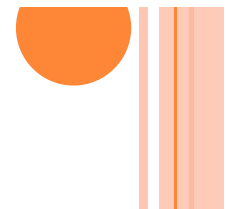
Remember the Nucleus

Mass number (number of protons plus neutrons)

Atomic number (number of protons or electrons)



- Remember that the nucleus is comprised of the **two nucleons, protons and neutrons**.
- The number of **protons is the atomic number**.
- The number of protons and neutrons together is effectively the **mass of the atom**.



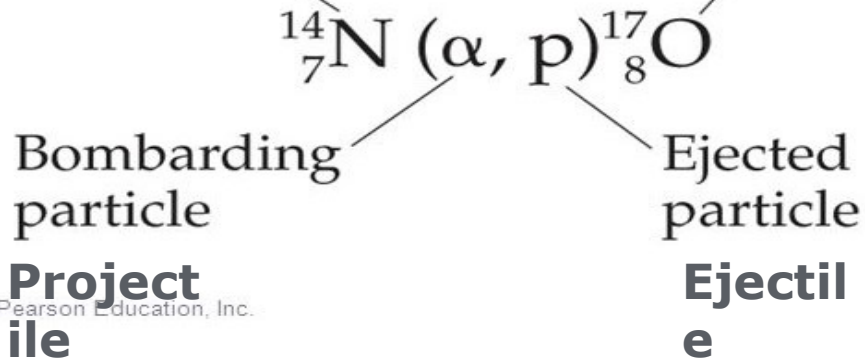
Writing Nuclear Equations for Nuclear Transmutations

Nuclear equations that represent nuclear transmutations are written two ways:



or

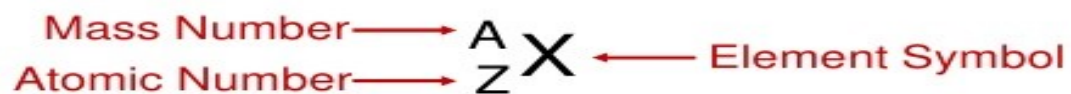
2) Target nucleus **Parent nucleus** Product nucleus **Daughter/Recoil nucleus**



Bethe's Notation

Atomic number (Z) = number of protons in nucleus

Mass number (A) = number of protons + number of neutrons
 = atomic number (Z) + number of neutrons



	proton ${}^1_1\text{p}$ or ${}^1_1\text{H}$	neutron ${}^1_0\text{n}$	electron ${}^0_{-1}\text{e}$ or ${}^0_{-1}\beta$	positron ${}^0_{+1}\text{e}$ or ${}^0_{+1}\beta$	α particle ${}^4_2\text{He}$ or ${}^4_2\alpha$
A	1	1	0	0	4
Z	1	0	-1	+1	2

Identity	Symbol	Charge	Mass (amu)
helium nucleus	α	+2	4.001506
electron	$-\beta$	-1	0.000549
Photon(gamma radiation)	γ	—	—
neutron	n	0	1.008665
proton	p	+1	1.007276
positron	$+\beta$	+1	0.000549

Balancing Nuclear Equations

1. Conserve mass number (A).

The sum of protons plus neutrons in the products must equal the sum of protons plus neutrons in the reactants.



$$235 + 1 = 138 + 96 + 2 \times 1$$

2. Conserve atomic number (Z) or nuclear charge.

The sum of nuclear charges in the products must equal the sum of nuclear charges in the reactants.



$$92 + 0 = 55 + 37 + 2 \times 0$$

Radioactive Decay

Radioactive decay results in the emission of either:

- an alpha particle (α),
- a negative beta particle (electron) (β^-),
- a positive beta particle (positron) (β^+),
- or a gamma ray (γ).

In a nuclear reaction the MASS and ATOMIC NUMBER must be the SAME on both sides of the equations

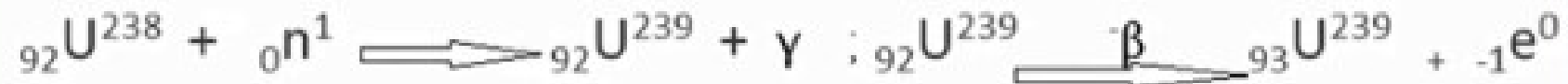
Summary

Reaction	What happens?	Mass #	Atomic #
Alpha Decay α	Lose Helium Nucleus	-4	-2
Beta Decay β^-	Lose electron from nucleus (neutron turns into proton)	No change	+1
Electron Capture	Gain electron in nucleus (proton turns into neutron)	No change	-1
Positron Emission β^+	Lose positron (proton turns into neutron)	No change	-1
Gamma Decay γ	Emit high energy gamma ray	No change	No change

Neutron Bombardments

- ▶ This process is carried out in a nuclear reactor which serves as a neutron source.
- ▶ Neutrons possess no charge and can readily bring about head on collision with nuclei of atoms.
- ▶ Such reactions are called as neutron reactions in which the neutron is captured by the nucleus of the atom.
- ▶ Neutron capture by a nucleus increases its neutron/proton ratio until the nucleus becomes unstable.
- ▶ Then a neutron is converted into a proton.
- ▶ This is followed by the emission of a β particle which gives rise to an element with atomic number higher by one unit.
- ▶ For example,

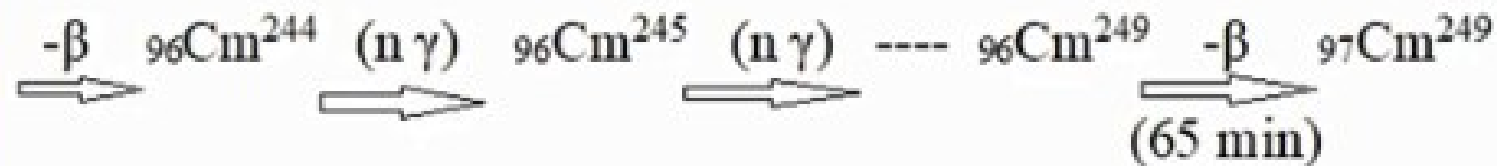
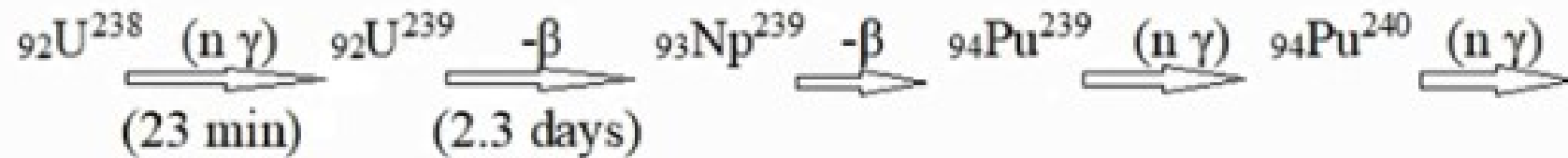
Neutron Bombardments



- The process of synthesis of transuranic elements involves capture of successive neutrons by (n, γ) process to produce nuclides that becomes unstable and hence suffer – β decay. This gives rise to an element with higher atomic number.

The general scheme for the transuranic elements can be represented as

Neutron Bombardments



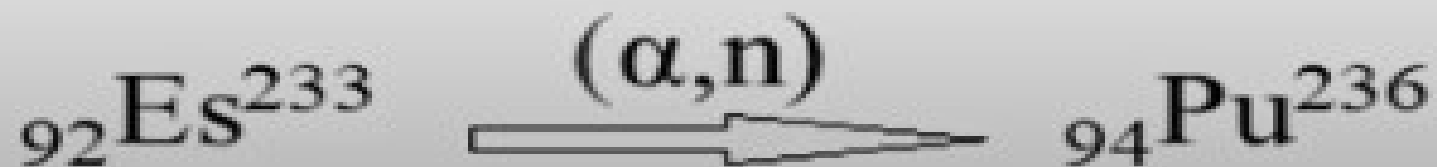
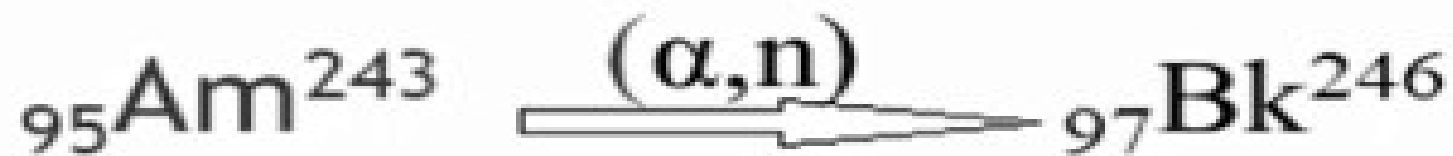
Neutron Bombardments

- Theoretically the synthesis of new elements can be continued until the neutron/proton ratio of the daughter element is too high to have a stable existence.
- The yield of heavier element is controlled by two factors-
 - 1) Half life of the isotopes
 - 2) By its ability to absorb neutrons

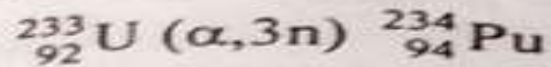
Bombardment with accelerated particles or High voltage nuclei

- ▶ The synthesis of transuranic elements may also be carried out by using accelerated projectiles (bombarding particles) such as α (${}_2\text{He}^4$), Proton (${}_1\text{P}^1$), Deuteron (${}_1\text{D}^2$). In this process of synthesis the nucleus captures the nuclei of these light elements (helium, proton, deuteron) and produces a new element of higher atomic number.
- ▶ The important projectile particles and their reactions are :
 (α, n) ; $(\alpha, 2n)$; $(\alpha, 3n)$; $(\alpha, 5n)$; $(\alpha, 7n)$; (D, n) ; $(D, 2n)$; $(D, 3n)$ etc.

(α , n) Reactions

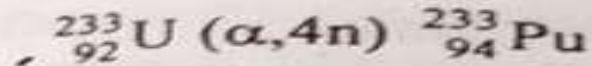


(c) (α , 3n) reactions -



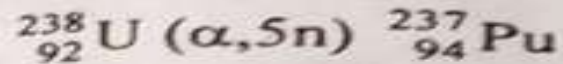
($t_{1/2} = 25 \text{ min.}$)

(d) (α , 4n) reactions -



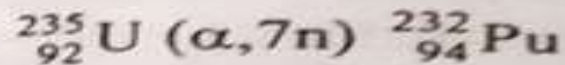
($t_{1/2} = 9 \text{ hrs.}$)

(e) (α , 5n) reactions -



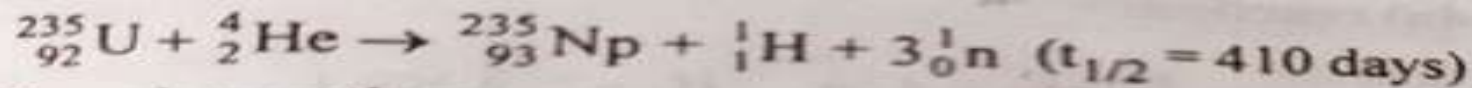
($t_{1/2} = 20 \text{ min.}$)

(f) (α , 7n) reactions -

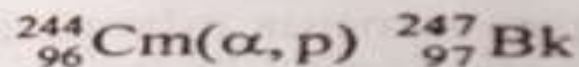


($t_{1/2} = 45.6 \text{ days}$)

(g) (α , p, 3n) reactions -



(h) (α , p) reactions -



($t_{1/2} = 7 \times 10^3 \text{ yrs.}$)

(i) (d, n) reactions -



($t_{1/2} = 22 \text{ hrs.}$)

(j) (d, 2n) reactions -



($t_{1/2} = 21 \text{ days}$)

(k) (d, 3n) reactions -



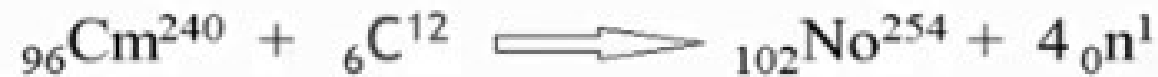
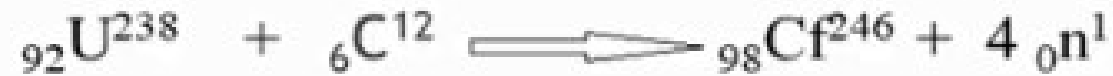
($t_{1/2} = 25 \text{ min.}$)

Heavy ion Bombardment

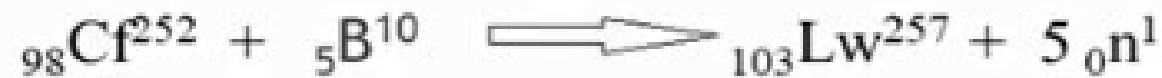
- ❖ The most commonly used heavy ion are obtained from the atoms of elements ${}_2\text{Be}^4$, ${}_6\text{C}^{12}$, ${}_7\text{N}^{14}$ and ${}_8\text{O}^{16}$.
- ❖ The ions are accelerated in a cyclotron and used to bombard the target element.
- ❖ In this type of nuclear reaction the target element receives in a single reaction much more mass and charge than by mere alpha or neutron bombardment.
- ❖ This method is particularly used for synthesizing heavier elements in which the target nucleus is bombarded with accelerated heavy ion particles. E.g.

Heavy ion Bombardment

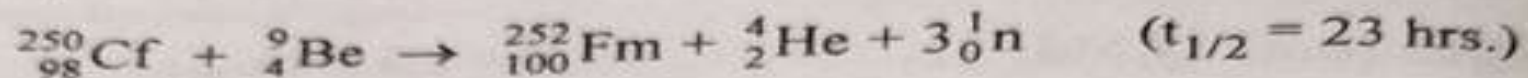
(${}_6\text{C}^{12}$, 3n)



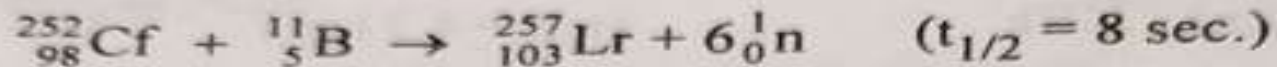
(${}_5\text{B}^{10}$, 5n)



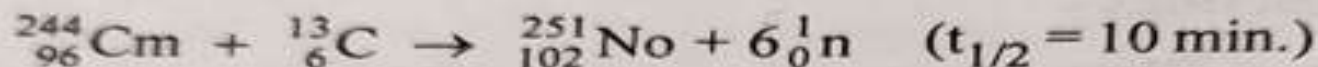
(a) (${}^9_4\text{Be}$, α , $3n$) reactions -



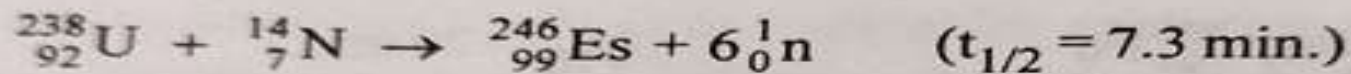
(b) (${}^{11}_5\text{B}$, $6n$) reactions -



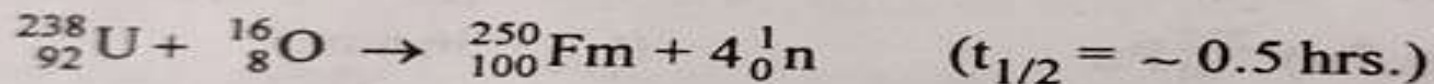
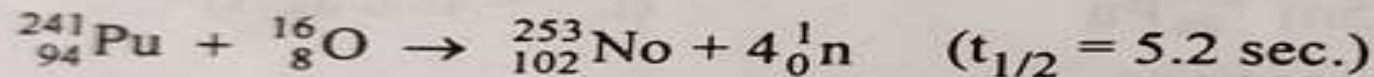
(c) (${}^{13}_6\text{C}$, $6n$) reactions -



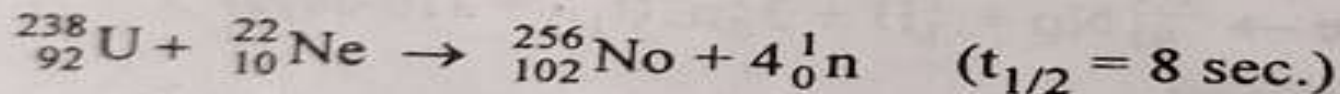
(d) (${}^{14}_7\text{N}$, $6n$) reactions -



(e) (${}^{16}_8\text{O}$, $4n$) reactions -



(f) (${}^{22}_{10}\text{Ne}$, $4n$) reactions -



IUPAC Nomenclature system for Super heavy elements

The Principles applied for deriving the names are

- ▶ The names should be short, systematic and obviously related to the atomic number of the elements
- ▶ The names should **end in 'ium'** irrespective of whether the element is expected to be metal or otherwise
- ▶ The symbols should **consists of three letters to avoid duplication** of some of the symbols already used for elements
- ▶ The symbols **should be derived directly from the atomic number** and be visually related to the names as far as possible.
- ▶ The system, for unknown elements does not deny the right of discoverer of new elements to propose other names to IUPAC after the discovery of new elements has been established beyond doubt in the scientific community.

IUPAC Nomenclature system for Super heavy elements

The nomenclature Rules

- 1) The name is derived directly from the atomic number of the element using the following **numerical roots for the three digits**

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

- 2) The roots are put together in the order of the digits which make up the atomic number and **terminated by -ium** to spell out the name.
- 3) The final **n** of **enn** is left out when it occurs before **nil** and the final **i** of **bi** and **tri** when it occurs before **-ium**.
- 4) The **symbol for the element is made from the first letter from the roots** which make up the name.
- 5) The mixture of Greek and Latin roots has choosed to avoid doubts. ³

IUPAC Nomenclature for Super heavy elements

At. No.	Name	Symbol	At. No.	Name	Symbol
101	un-nil-unium	Unu	120	un-bi-nilium	Ubn
102	un-nil-bium	Unb	121	un-bi-unium	Ubu
103	un-nil-trium	Unt	130	un-tri-nilium	Utn
104	un-nil-quadium	Unq	140	un-quad-nilium	Uqn
105	un-nil-pentium	Unp	150	un-pent-nilium	Upn
106	un-nil-hexium	Unh	200	bi-nil-nilium	Bnn
107	un-nil-septium	Uns	202	bi-nil-bium	Bnb
108	un-nil-octium	Uno	300	tri-nil-nilium	Tnn
109	un-nil-ennium	Une	550	pent-pent-nilium	Ppn
110	un-nil-nilium	Unn	679	hex-sept-ennium	Hse
111	un-un-unium	Unu	869	oct-hex-ennium	Ohe
112	un-un-bium	Uub	999	enn-enn-ennium	Eee

Thank You

