→ **f-Block elements : Introduction :** →

- Those elements in which last e⁻ (differentiating electron) enters in to f-subshell are called f-block elements.
- last e⁻ enters in anti-penultimate shell [i.e. (n-2)th Shell] or [(n-2)f subshell]
- also called inner-transition elements.
- Valence shell (संयोजी कोश) electronic configuration is $(n-2)f^{0-14}\ (n-1)d^{0-2}.\ ns^2$
- These elements have been shown at a separate place at the bottom of the periodic table.

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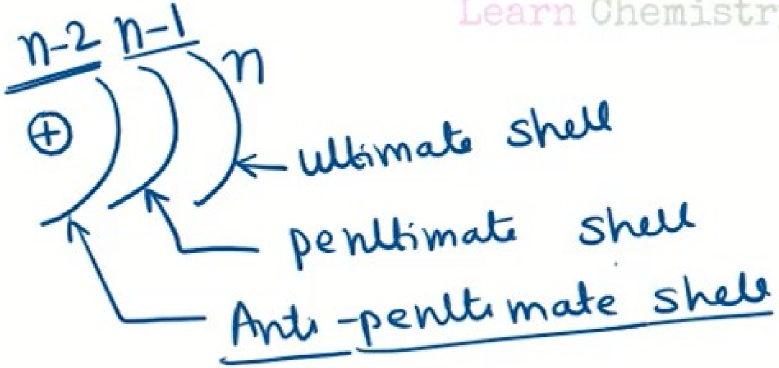

→ Classification of f-block elements :→

(i) Lanthenide Series

- 14 elements [$_{58}Ce$ to $_{71}Lu$]
- Lanthenides, Lanthanones, rare earth (दुर्लभ मृदा), 4f block elements.
- **Lanthenides** :- they are placed after lanthanum ($_{57}La$) in group 3 and period 6 and show close similarities with La.
- **Rare earth** :- originally extracted from oxides for which ancient name was earth and were considered as rare. the term rare earth is avoided now because many of these are no longer rare but are abundant (प्रचुर)
- Lanthenides are present in 6th period, these elements have six shell (कोश) in their electronic confi. thus last e^- enters in $(6-2)f$ or 4f sub-shell.
- Lanthenides are a series of 14 elements in which last e^- goes to 4f - sub shell or f sub-shell of 4th shell
- 15 elements have similar properties. Hence the study of lanthenides consists of the study of 15 elements (La to Lu)
- La is prototype (आद्यरूप, मूल रूप) of Lanthenides.

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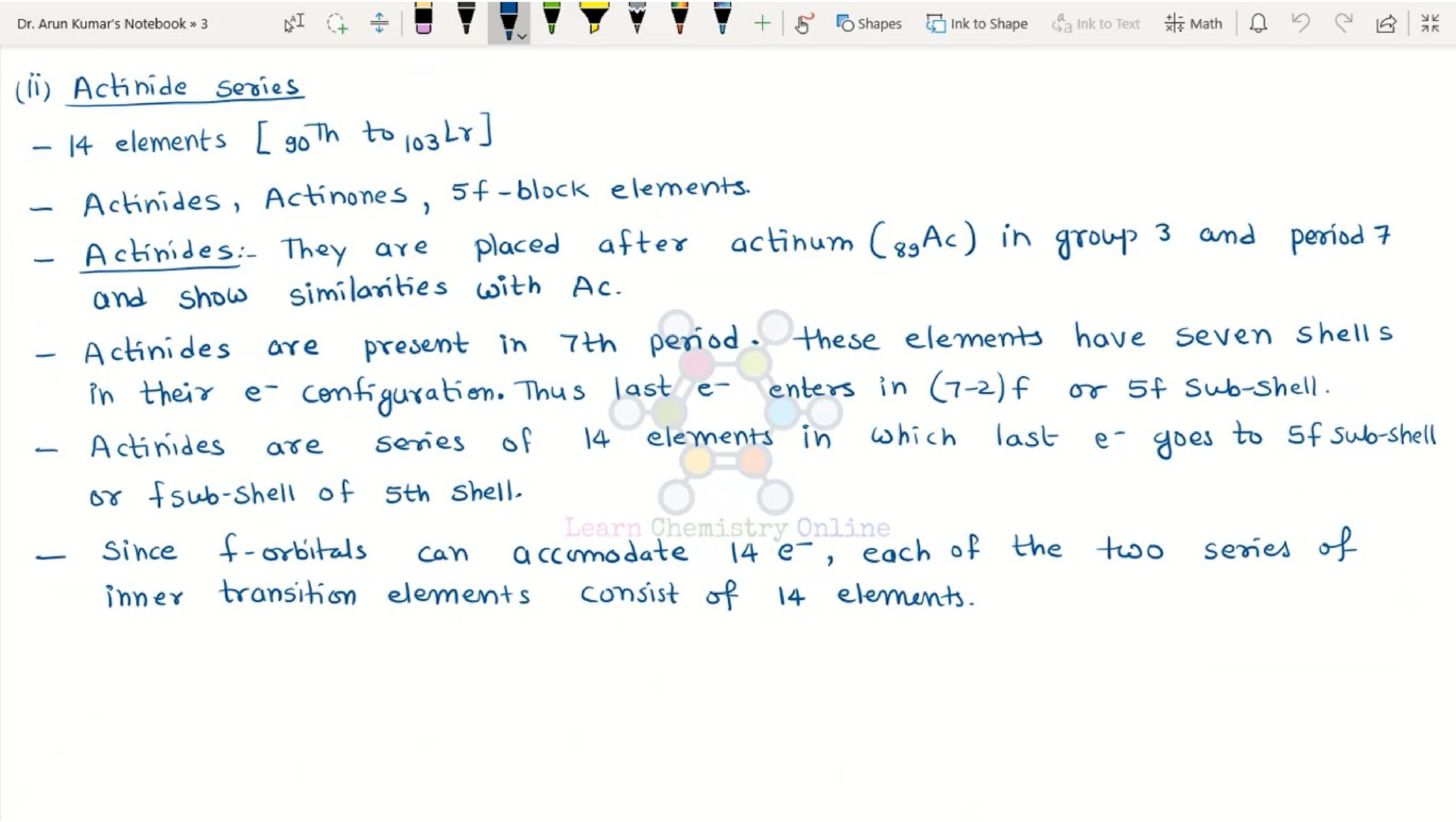

(ii) Actinide series

- 14 elements [$_{90}Th$ to $_{103}Lr$]
- Actinides, Actinones, 5f-block elements.
- Actinides:- They are placed after actinum ($_{89}Ac$) in group 3 and period 7 and show similarities with Ac.
- Actinides are present in 7th period. these elements have seven shells in their e⁻ configuration. Thus last e⁻ enters in (7-2)f or 5f Sub-shell.
- Actinides are series of 14 elements in which last e⁻ goes to 5f Sub-shell or f sub-shell of 5th shell.
- Since f-orbitals can accomodate 14 e^-, each of the two series of inner transition elements consist of 14 elements.

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(i) Lanthenide series

1	Lanthanum	La	57
2	Cerium	Ce	58
3	Praseodymium	Pr	59
4	Neodymium	Nd	60
5	Promethium	Pm	61
6	Samarium	Sm	62
7	Europium	Eu	63
8	Gadolinium	Gd	64
9	Terbium	Tb	65
10	Dysprosium	Dy	66
11	Holmium	Ho	67
12	Erbium	Er	68
13	Thulium	Tm	69
14	Ytterbium	Yb	70
15	Lutetium	Lu	71

(ii) Actinide series

1	Actinum	Ac	89
2	Thorium	Th	90
3	Protactinium	Pa	91
4	Uranium	U	92
5	Neptunium	Np	93
6	Plutonium	Pu	94
7	Americium	Am	95
8	Curium	Cm	96
9	Berklium	Bk	97
10	Californium	Cf	98
11	Einsteinium	Es	99
12	Fermium	Fm	100
13	Mendelevium	Md	101
14	Nobelium	No	102
15.	Lawrencium	Lr	103

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→ Electronic configuration of Lanthanides :→

	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Element	La	*Ce	Pr	Nd	Pm	Sm	Eu	*Gd	Tb	Dy	Ho	Er	Tm	Yb	*Lu
Z	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Noblegas	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe]	[xe] → 54
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

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→ **E.C. of Lanthanum (La)** :→ ⑤⑦ → (Ba) → ⑤⑥ → $\boxed{6s^2}$ → 4f

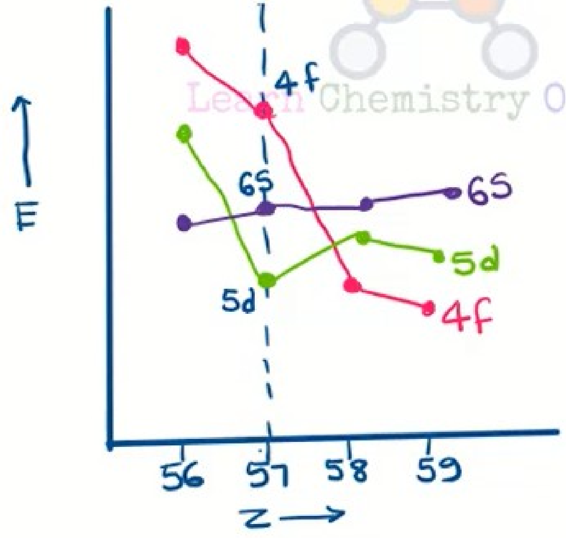
- After completion of 6s orbital of $_{56}$Ba in 6th period. e⁻ should enters into 4f orbital to give [Xe] $4f^1 5d^0 6s^2$ E.C. (as per Aufbau principle)

n+l Rule 4f → 4 + 3 = 7

5d → 5 + 2 = 7

✱ but e⁻ enters into 5d instead of 4f in La. because energy of 5d is lower than that of 4f orbitals.

✱ So. E.C. of La is [Xe] $4f^0 5d^1 6s^2$ (against Aufbau principle)



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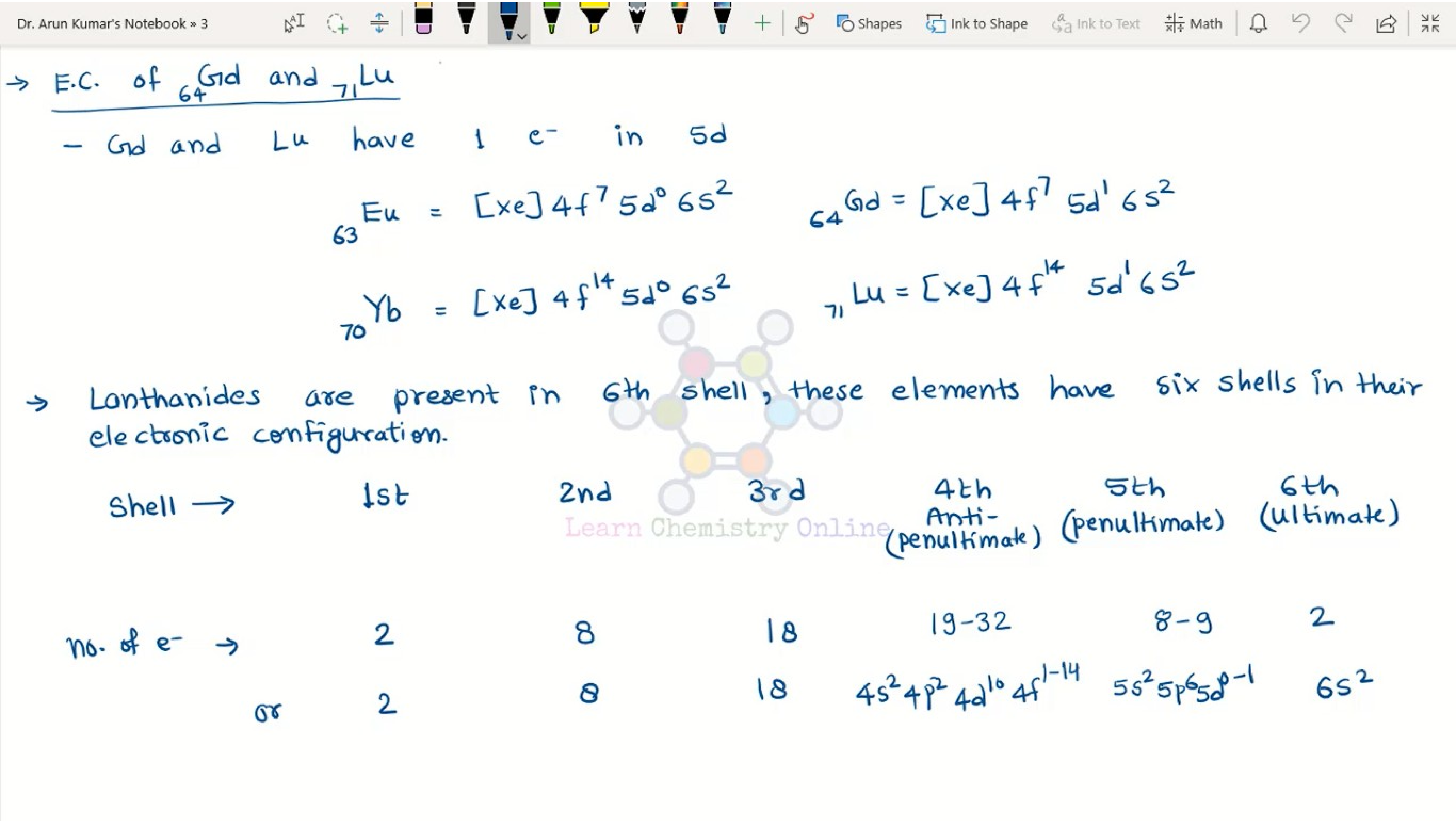

→ E.C. of $_{64}Gd$ and $_{71}Lu$

– Gd and Lu have 1 e⁻ in 5d

$_{63}Eu$ = $[Xe]\,4f^7\,5d^0\,6s^2$ $_{64}Gd$ = $[Xe]\,4f^7\,5d^1\,6s^2$

$_{70}Yb$ = $[Xe]\,4f^{14}\,5d^0\,6s^2$ $_{71}Lu$ = $[Xe]\,4f^{14}\,5d^1\,6s^2$

→ Lanthanides are present in 6th shell, these elements have six shells in their electronic configuration.

Shell →	1st	2nd	3rd	4th Anti-(penultimate)	5th (penultimate)	6th (ultimate)
no. of e⁻ →	2	8	18	19-32	8-9	2
or	2	8	18	$4s^2 4p^2 4d^{10} 4f^{1-14}$	$5s^2 5p^6 5d^{0-1}$	$6s^2$

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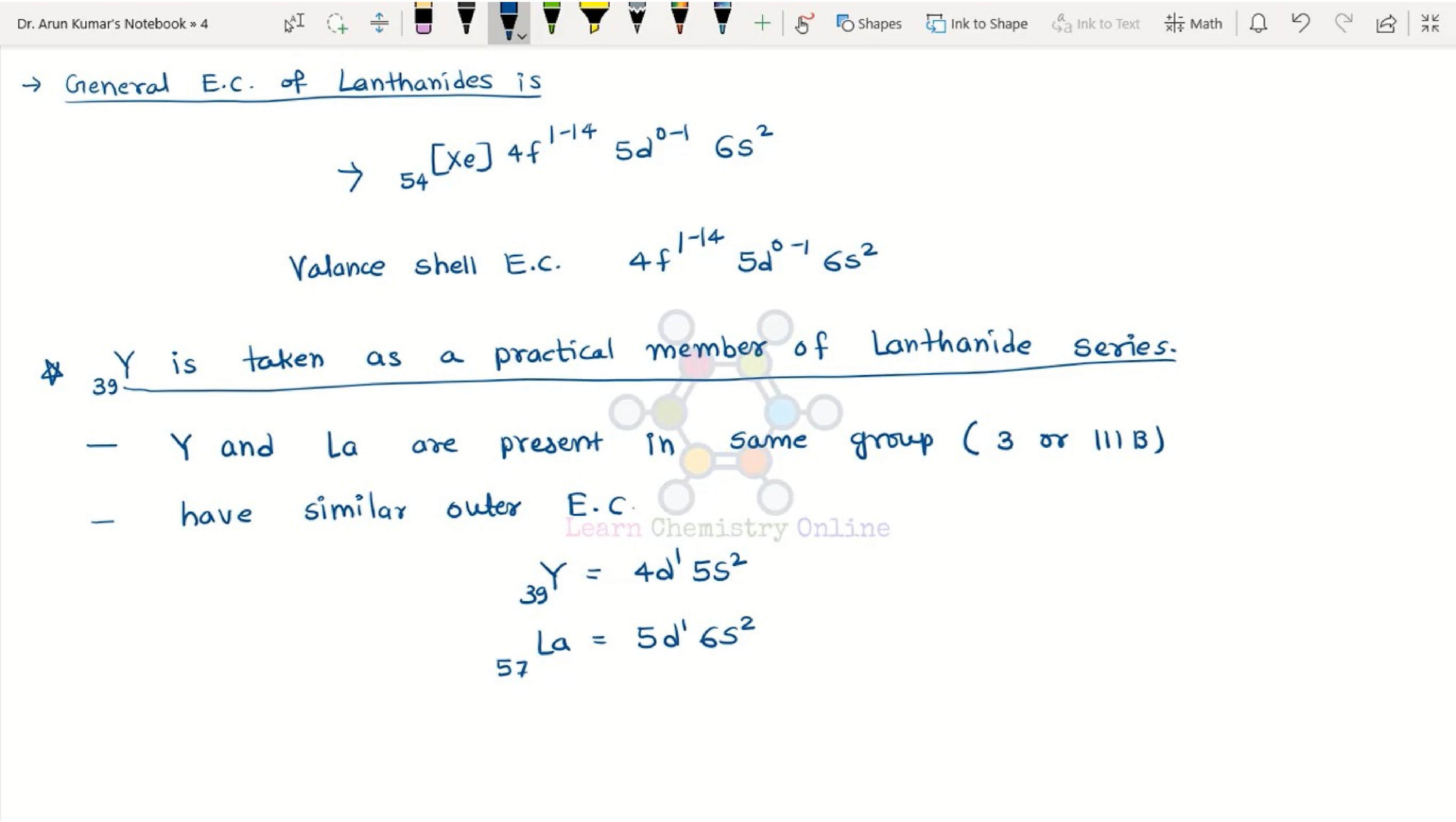

→ General E.C. of Lanthanides is

→ $_{54}[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^{2}$

Valance shell E.C. $4f^{1-14}\ 5d^{0-1}\ 6s^{2}$

✡ $_{39}Y$ is taken as a practical member of Lanthanide series.

— Y and La are present in same group (3 or III B)

— have similar outer E.C.

$_{39}Y = 4d^{1}\ 5s^{2}$

$_{57}La = 5d^{1}\ 6s^{2}$

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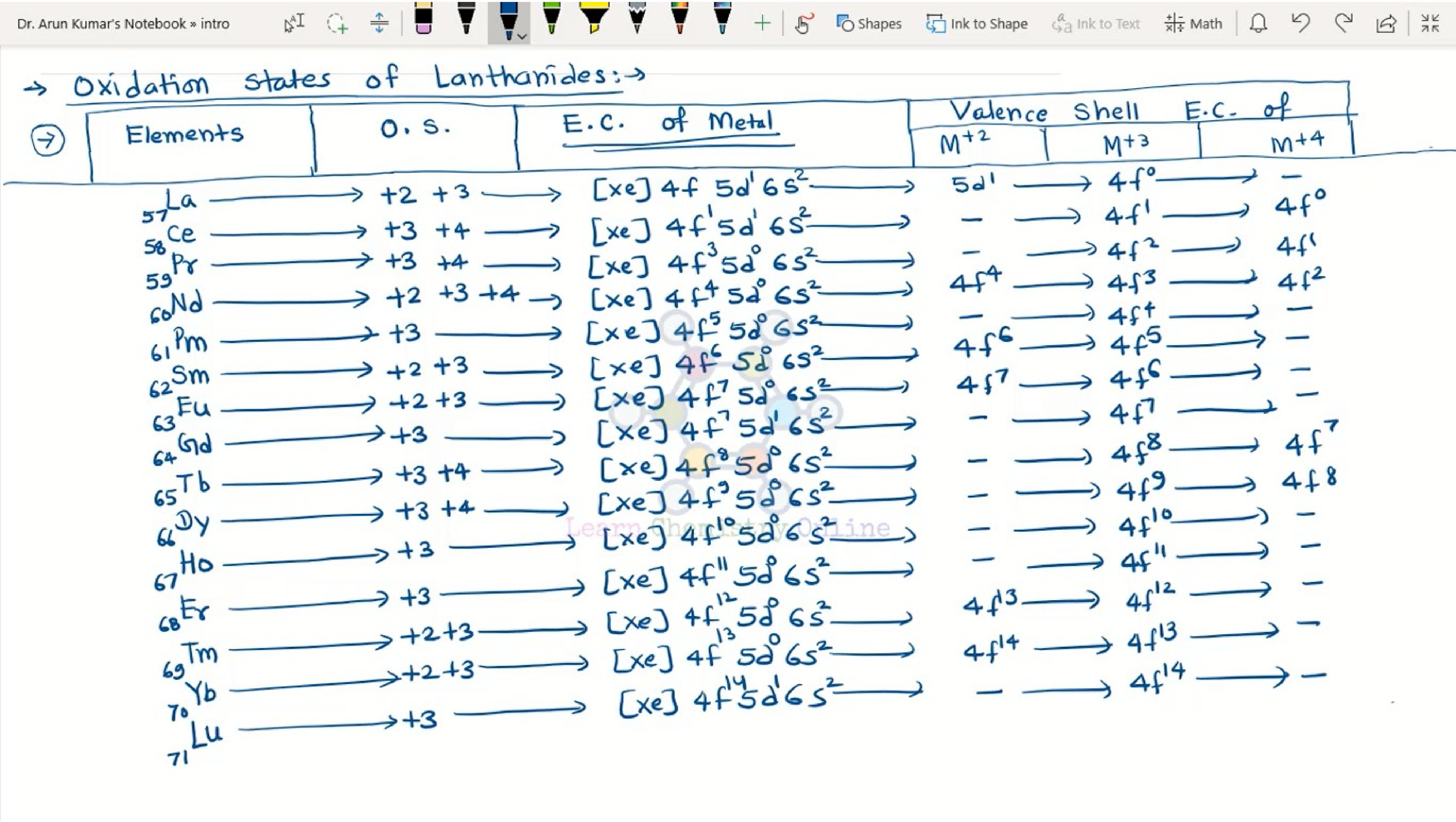

→ Oxidation states of Lanthanides:→

⑦

Elements	O. S.	E.C. of Metal	Valence Shell E.C. of		
			M^{+2}	M^{+3}	M^{+4}
$_{57}La$ →	→ $+2\ +3$ →	$[xe]\,4f\,5d^1\,6s^2$ →	$5d^1$ →	$4f^0$ →	—
$_{58}Ce$ →	→ $+3\ +4$ →	$[xe]\,4f^1\,5d^1\,6s^2$ →	— →	$4f^1$ →	$4f^0$
$_{59}Pr$ →	→ $+3\ +4$ →	$[xe]\,4f^3\,5d^0\,6s^2$ →	— →	$4f^2$ →	$4f^1$
$_{60}Nd$ →	→ $+2\ +3\ +4$ →	$[xe]\,4f^4\,5d^0\,6s^2$ →	$4f^4$ →	$4f^3$ →	$4f^2$
$_{61}Pm$ →	→ $+3$ →	$[xe]\,4f^5\,5d^0\,6s^2$ →	— →	$4f^4$ →	—
$_{62}Sm$ →	→ $+2\ +3$ →	$[xe]\,4f^6\,5d^0\,6s^2$ →	$4f^6$ →	$4f^5$ →	—
$_{63}Eu$ →	→ $+2\ +3$ →	$[xe]\,4f^7\,5d^0\,6s^2$ →	$4f^7$ →	$4f^6$ →	—
$_{64}Gd$ →	→ $+3$ →	$[xe]\,4f^7\,5d^1\,6s^2$ →	— →	$4f^7$ →	—
$_{65}Tb$ →	→ $+3\ +4$ →	$[xe]\,4f^8\,5d^0\,6s^2$ →	— →	$4f^8$ →	$4f^7$
$_{66}Dy$ →	→ $+3\ +4$ →	$[xe]\,4f^9\,5d^0\,6s^2$ →	— →	$4f^9$ →	$4f^8$
$_{67}Ho$ →	→ $+3$ →	$[xe]\,4f^{10}\,5d^0\,6s^2$ →	— →	$4f^{10}$ →	—
$_{68}Er$ →	→ $+3$ →	$[xe]\,4f^{11}\,5d^0\,6s^2$ →	— →	$4f^{11}$ →	—
$_{69}Tm$ →	→ $+2+3$ →	$[xe]\,4f^{12}\,5d^0\,6s^2$ →	$4f^{13}$ →	$4f^{12}$ →	—
$_{70}Yb$ →	→ $+2+3$ →	$[xe]\,4f^{13}\,5d^0\,6s^2$ →	$4f^{14}$ →	$4f^{13}$ →	—
$_{71}Lu$ →	→ $+3$ →	$[xe]\,4f^{14}\,5d^1\,6s^2$ →	— →	$4f^{14}$ →	—

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→ **+3 oxidation state :→**

- This is most stable oxidation state
- La → [xe] $4f^0 5d^1 6s^2$ → La^{+3} → [xe] $4f^0 5d^0 6s^0$ → higher than +3 is not possible.
- $_{64}Gd$ → [xe] $4f^7 5d^1 6s^2$ → Gd^{+3} → [xe] $4f^7 5d^0 6s$ → Stable due to half filled
- $_{71}Lu$ → [xe] $4f^{14} 5d^1 6s^2$ → Lu^{+3} → [xe] $4f^{14} 5d^0 6s$ → Stable due to full filled
- other Lanthanides also shows +3 Oxidation states but do not contain $4f^0$ or $4f^7$ or $4f^{14}$ orbitals.

example Ce^{+3} = [xe] $4f^1$ Pr^{+3} = [xe] $4f^2$

* stability of +3 O.S. can not be explained on the basis of stability associated with $4f^0$ or $4f^7$ or $4f^{14}$ configuration.

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→ +2 and +4 oxidation states :→

- +2 and +4 oxidation states are less stable than +3 O.S.

- $Eu^{+2} = [Xe]\,4f^7$

  $Ce^{+4} = [Xe]\,4f^0$

  $Yb^{+2} = [Xe]\,4f^{14}$

  $Tb^{+4} = [Xe]\,4f^7$

  } Contain $4f^0$ or $4f^7$ or $4f^{14}$ configuration

- $Ce^{+2} = [Xe]\,4f^2$

  $Sm^{+2} = [Xe]\,4f^6$

  $Pr^{+4} = [Xe]\,4f^1$

  $Dy^{+4} = [Xe]\,4f^8$

  $Nd^{+2} = [Xe]\,4f^4$

  $Tm^{+2} = [Xe]\,4f^{13}$

  $Nd^{+4} = [Xe]\,4f^2$

  } do not contain $4f^0$ or $4f^7$ or $4f^{14}$ configuration

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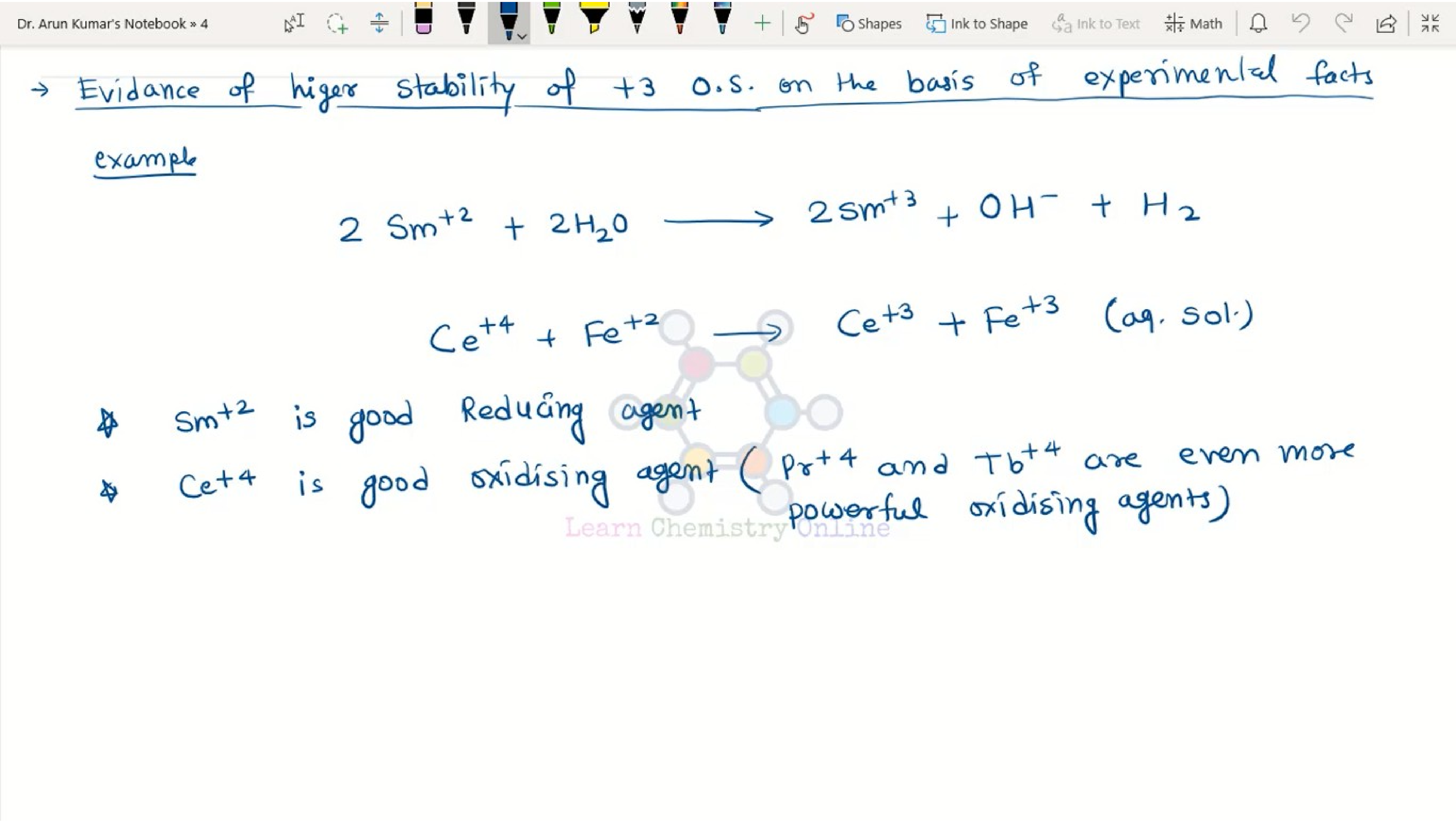
- +2 and +4 oxidation state of many lanthanides can be explained on the basis of $4f^0$ or $4f^7$ or $4f^{14}$ configuration. but +2 and +4 O. states of some lanthanides can not be explained on the basis of $4f^0$ or $4f^7$ or $4f^{14}$ c.

- In case of these elements, their oxidation states are explained on the basis of highly complicated thermodynamic and kinetic factors.



→ Evidance of higer stability of +3 O.S. on the basis of experimental facts

example

$$2\,Sm^{+2} + 2H_2O \longrightarrow 2Sm^{+3} + OH^- + H_2$$

$$Ce^{+4} + Fe^{+2} \longrightarrow Ce^{+3} + Fe^{+3} \text{ (aq. sol.)}$$

- Sm^{+2} is good Reducing agent
- Ce^{+4} is good oxidising agent (Pr^{+4} and Tb^{+4} are even more powerful oxidising agents)

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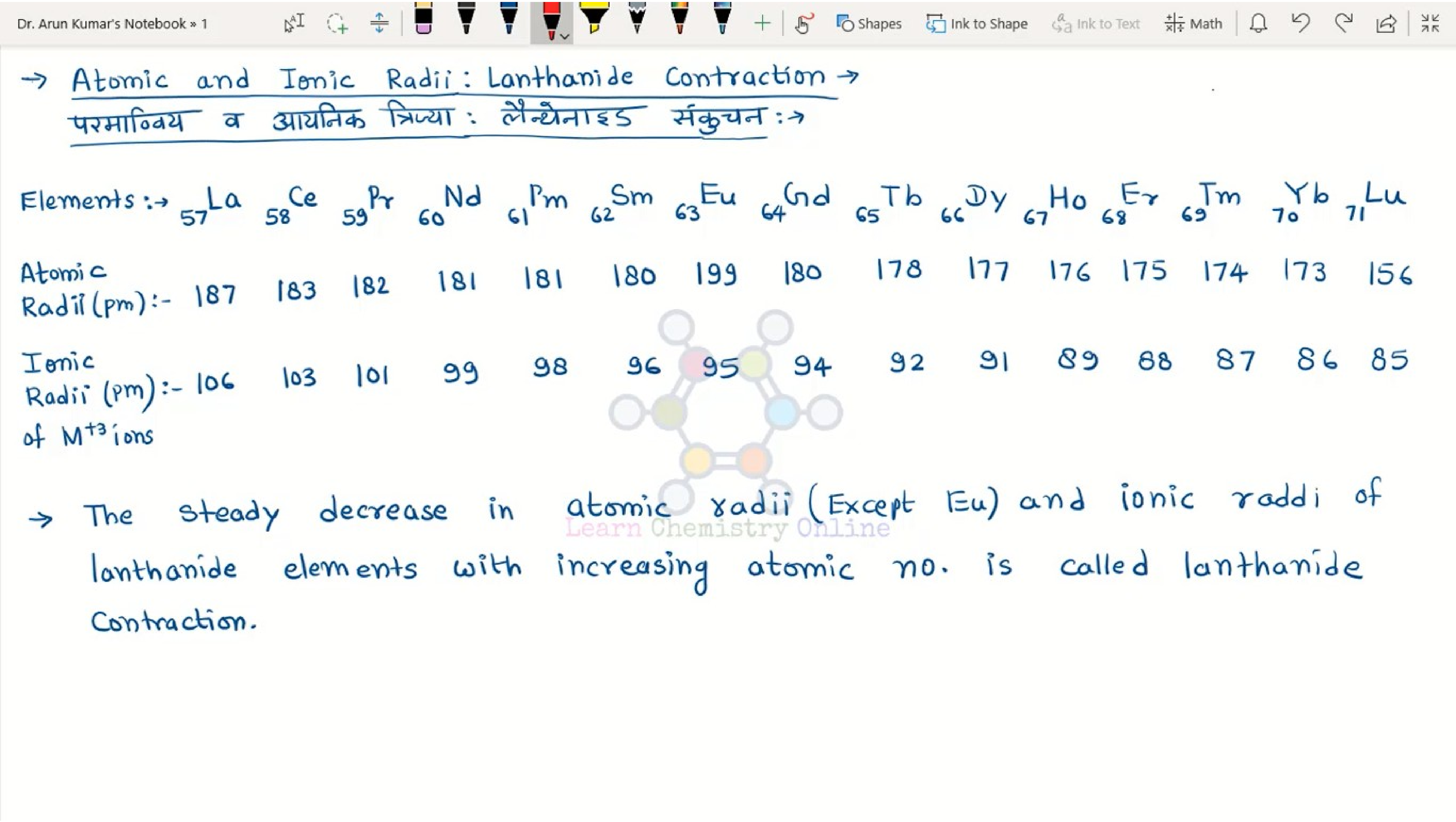

→ Atomic and Ionic Radii : Lanthanide Contraction →
परमाण्विय व आयनिक त्रिज्या : लैन्थेनाइड संकुचन :→

Elements :→	$_{57}La$	$_{58}Ce$	$_{59}Pr$	$_{60}Nd$	$_{61}Pm$	$_{62}Sm$	$_{63}Eu$	$_{64}Gd$	$_{65}Tb$	$_{66}Dy$	$_{67}Ho$	$_{68}Er$	$_{69}Tm$	$_{70}Yb$	$_{71}Lu$
Atomic Radii (pm) :-	187	183	182	181	181	180	199	180	178	177	176	175	174	173	156
Ionic Radii (pm) :- of M^{+3} ions	106	103	101	99	98	96	95	94	92	91	89	88	87	86	85

→ The steady decrease in atomic radii (Except Eu) and ionic raddi of lanthanide elements with increasing atomic no. is called lanthanide Contraction.

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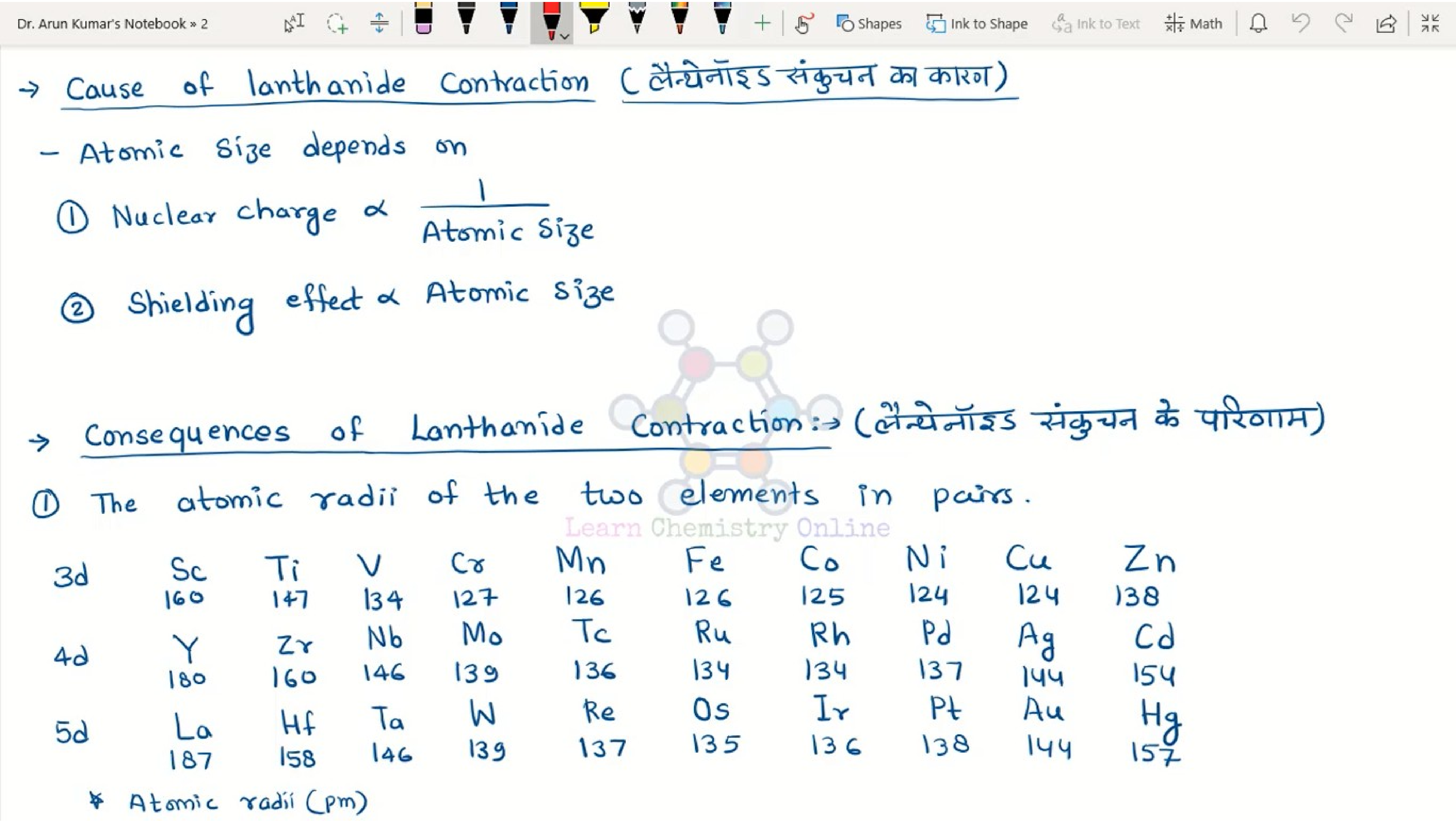

→ **Cause of lanthanide Contraction (लैन्थेनॉइड संकुचन का कारण)**

– Atomic Size depends on

① Nuclear charge $\propto \frac{1}{\text{Atomic Size}}$

② Shielding effect $\propto$ Atomic Size

→ **Consequences of Lanthanide Contraction :→ (लैन्थेनॉइड संकुचन के परिणाम)**

① The atomic radii of the two elements in pairs.

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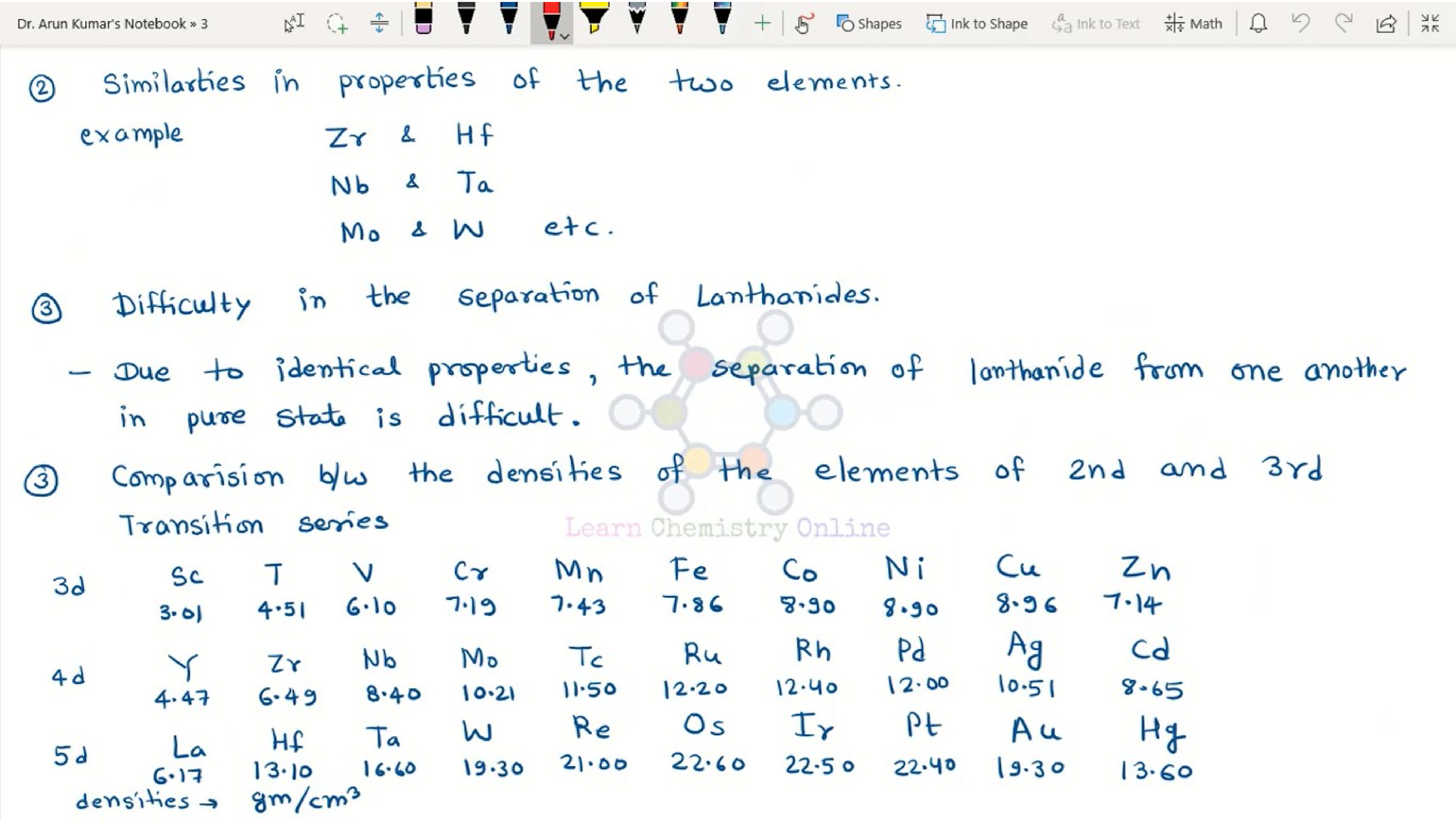
3d	Sc 160	Ti 147	V 134	Cr 127	Mn 126	Fe 126	Co 125	Ni 124	Cu 124	Zn 138
4d	Y 180	Zr 160	Nb 146	Mo 139	Tc 136	Ru 134	Rh 134	Pd 137	Ag 144	Cd 154
5d	La 187	Hf 158	Ta 146	W 139	Re 137	Os 135	Ir 136	Pt 138	Au 144	Hg 157

* Atomic radii (pm)



② Similarties in properties of the two elements.

example
Zr & Hf
Nb & Ta
Mo & W etc.

③ Difficulty in the separation of Lanthanides.

- Due to identical properties, the separation of lanthanide from one another in pure State is difficult.

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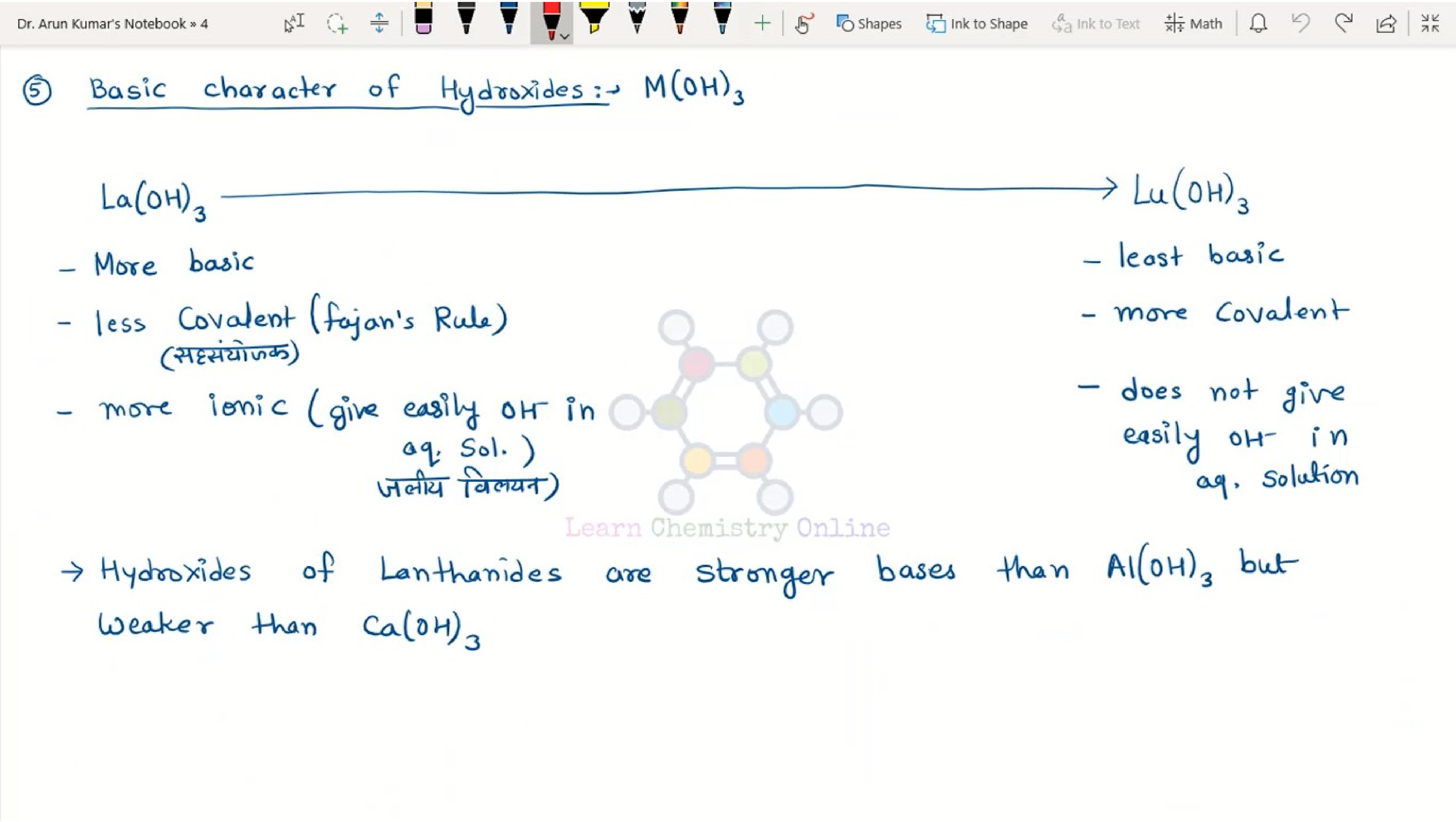
③ Comparision b/w the densities of the elements of 2nd and 3rd Transition series

3d	Sc 3·01	T 4·51	V 6·10	Cr 7·19	Mn 7·43	Fe 7·86	Co 8·90	Ni 8·90	Cu 8·96	Zn 7·14
4d	Y 4·47	Zr 6·49	Nb 8·40	Mo 10·21	Tc 11·50	Ru 12·20	Rh 12·40	Pd 12·00	Ag 10·51	Cd 8·65
5d	La 6·17	Hf 13·10	Ta 16·60	W 19·30	Re 21·00	Os 22·60	Ir 22·50	Pt 22·40	Au 19·30	Hg 13·60

densities → gm/cm^3



⑤ Basic character of Hydroxides :→ $M(OH)_3$

$La(OH)_3 \longrightarrow Lu(OH)_3$

- More basic
- less Covalent (Fajan's Rule)
  (सहसंयोजक)
- more ionic (give easily OH^- in aq. Sol.)
  (जलीय विलयन)

- least basic
- more Covalent
- does not give easily OH^- in aq. Solution

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→ Hydroxides of Lanthanides are stronger bases than $Al(OH)_3$ but weaker than $Ca(OH)_3$

→ Colour of Tripositive Lanthanide ions (M^{+3} ions) :→

- Most of trivalent (त्रिसंयोजी धनायन) Cations of lanthanide elements are coloured in the Solid as well as in aqueous solution (जलीय विलयन) while only few are Colourless.
- The Colour depends on no. of unpaired e^- (n) present in 4f orbitals.

→ rigin of Colour (रंग की उत्पत्ति) :→

- Colour of lanthanide tripositive (त्रिधनात्मक) ions is due to f-f transition.
- Colour of the ions in their compounds arise due to absorption of light in visible region (दृश्य क्षेत्र). Colourless ions absrob in UV or IR region.
- This results in the transition of electrons of the ions from the lower energy 4f-orbitals to the higher energy 4f orbitals.
- Thus Lanthanides ions have colour which is complementary to the Colour of absorbed light

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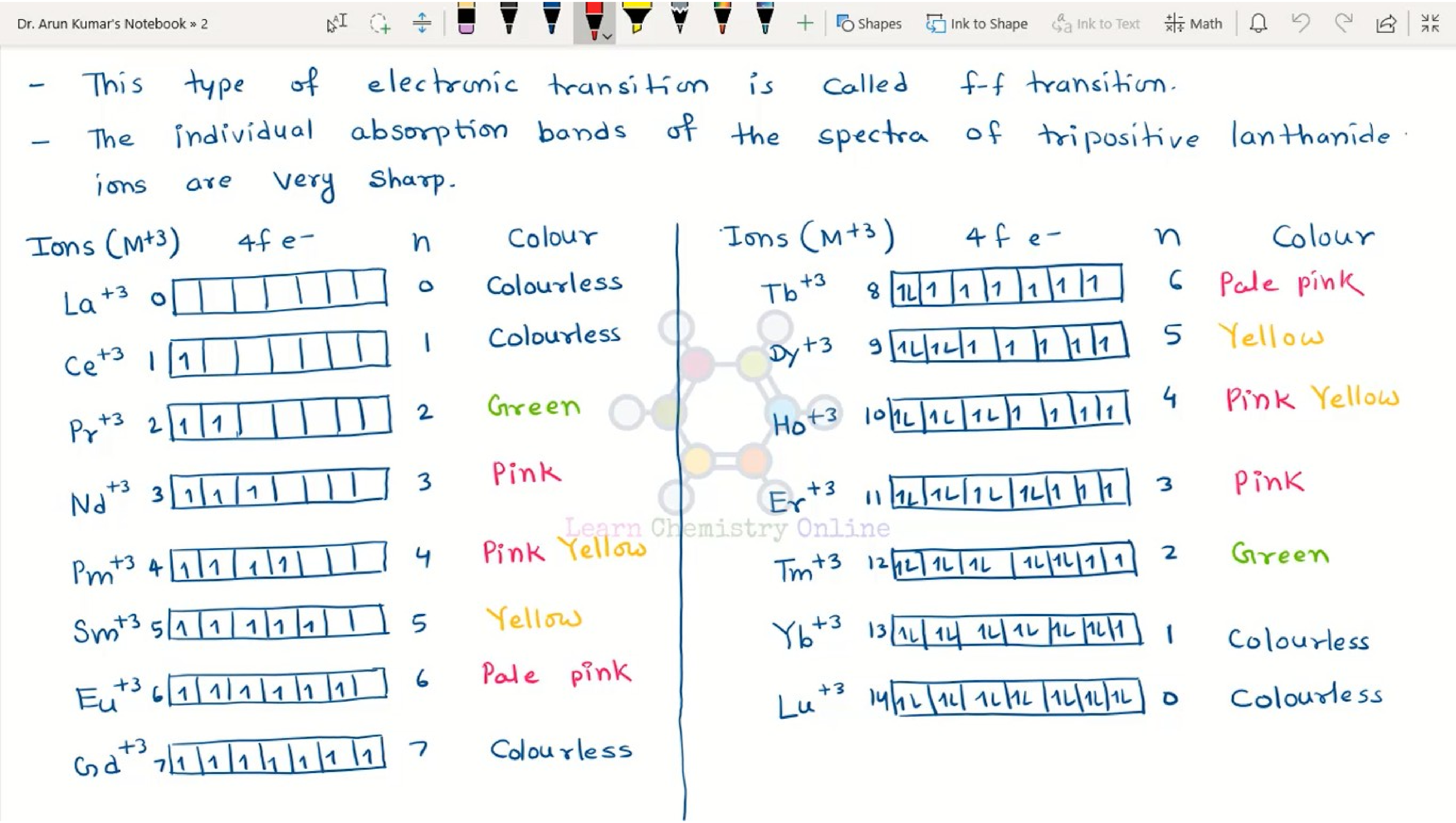

- This type of electronic transition is called f-f transition.
- The individual absorption bands of the spectra of tripositive lanthanide ions are very sharp.

Ions (M^{+3})	4f e-		n	Colour
La^{+3}	0	□ □ □ □ □ □ □	0	Colourless
Ce^{+3}	1	↿ □ □ □ □ □ □	1	Colourless
Pr^{+3}	2	↿ ↿ □ □ □ □ □	2	Green
Nd^{+3}	3	↿ ↿ ↿ □ □ □ □	3	Pink
Pm^{+3}	4	↿ ↿ ↿ ↿ □ □ □	4	Pink Yellow
Sm^{+3}	5	↿ ↿ ↿ ↿ ↿ □ □	5	Yellow
Eu^{+3}	6	↿ ↿ ↿ ↿ ↿ ↿ □	6	Pale pink
Gd^{+3}	7	↿ ↿ ↿ ↿ ↿ ↿ ↿	7	Colourless
Tb^{+3}	8	↿⇂ ↿ ↿ ↿ ↿ ↿ ↿	6	Pale pink
Dy^{+3}	9	↿⇂ ↿⇂ ↿ ↿ ↿ ↿ ↿	5	Yellow
Ho^{+3}	10	↿⇂ ↿⇂ ↿⇂ ↿ ↿ ↿ ↿	4	Pink Yellow
Er^{+3}	11	↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿ ↿ ↿	3	Pink
Tm^{+3}	12	↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿ ↿	2	Green
Yb^{+3}	13	↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿	1	Colourless
Lu^{+3}	14	↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂	0	Colourless

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- Charge transfer (आवेश स्थानान्तरण) phenomenon is also observed in some lanthanide ions.

<u>example</u> :- orange-red colour of Ce^{+4} ($L \rightarrow M$)
Yellow Colour of Eu^{+3} ($M \rightarrow L$)

→ <u>Comparision b/w d-d transition and f-f transition</u> :→

- f-f transitions are more forbidden (वर्जित) than d-d transitions.
- because 4f e^- are much less affected by ligand e^- than the e^- in d orbitals of transition metal ions in their complexes.
- Hence selection rule (चयन नियम) are more strictly followed for transition in the compounds of lanthanides than in the compounds of transition metals (संक्रमण धातु)

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→ Formation of complex (संकुल) by lantanides :→

- lanthanides cation have high charge (+3) but due to their large size they have less tendency to form complexes
- Most common ligands, which form Complexes with M^{+3} cations are –

ⓐ Chelating oxygen containing ligands

example :- EDTA, Citric acid, oxalic acid, acetylacetone etc.

ⓑ Nitrogen containing ligands

example :- Ethylenediamine, NCS etc.

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- Bonding b/w M^{+3} ions and ligands depends on electronegativity (विद्युतऋणता) of donor atom of ligand
- order of bond formation with monodentate ligand –

$F^- < OH^- < H_2O < NO_3^- < Cl^-$ etc.

- Complex formation in aq. solution (जलीय विलयन) is possible only with those ligands which binds to metal through O-atom. Due to resonating structures, (अनुनादी संरचनाएँ) the chelate ring stablised and cannot be replaced by OH^- and H_2O.

- If the complexes in which the ligands are bondend to the metal through N and S dissociates in aq. Solution. (these complexes are prepared in non-aq. Solutions)

- Coordination number (समन्वय संख्या)
  - → ranges from 6 to 9
  - → max. C.N. with monodentate → 9
  - → ,, C.N. with bidentate → 6,7,8

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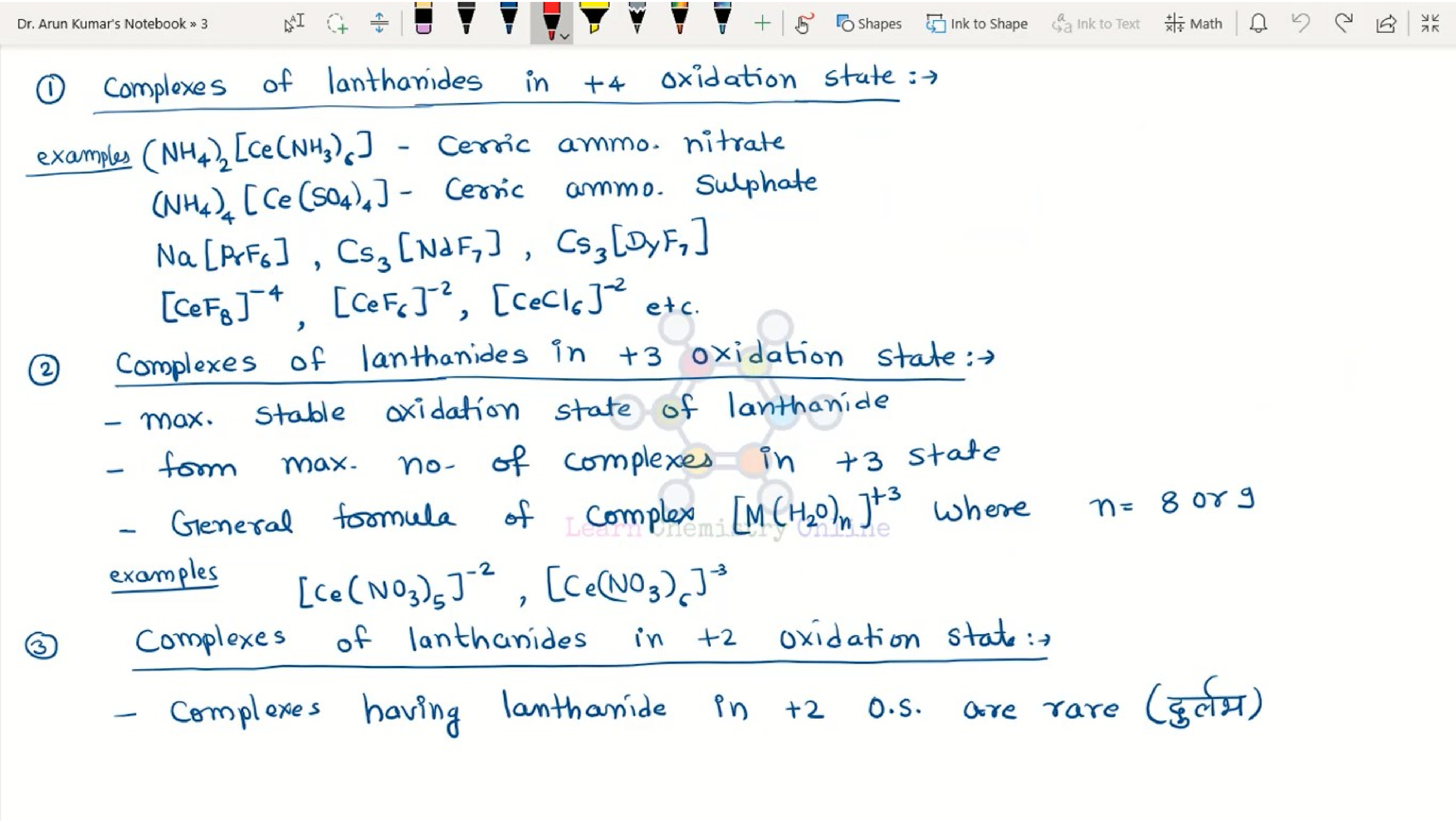

① Complexes of lanthanides in +4 oxidation state :→

examples $(NH_4)_2[Ce(NH_3)_6]$ - Cerric ammo. nitrate

$(NH_4)_4[Ce(SO_4)_4]$ - Cerric ammo. Sulphate

$Na[PrF_6]$, $Cs_3[NdF_7]$, $Cs_3[DyF_7]$

$[CeF_8]^{-4}$, $[CeF_6]^{-2}$, $[CeCl_6]^{-2}$ etc.

② Complexes of lanthanides in +3 oxidation state :→

- max. stable oxidation state of lanthanide
- form max. no. of complexes in +3 state
- General formula of complex $[M(H_2O)_n]^{+3}$ where $n = 8$ or 9

examples $[Ce(NO_3)_5]^{-2}$, $[Ce(NO_3)_6]^{-3}$

③ Complexes of lanthanides in +2 oxidation state :→

- Complexes having lanthanide in +2 O.S. are rare (दुर्लभ)

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→ Magnetic properties of Tripositive Lanthanide ions (M^{+3} ions):→

त्रिधनात्मक लैन्थनाइड आयनों के चुम्बकीय गुण:→

- The Magnetic properties of tripositive Lanthanide ions is due to 4f e^-.
- e^- generates magnetic moment (चु० आघूर्ण) due to two types of motion –

ⓐ orbital motion (कक्षकीय गति)

- orbital motion generates orbital magnetic moment (कक्षकीय चु० आघूर्ण)

ⓑ spin motion (चक्रण गति)

- spin motion generates spin magnetic moment (चक्रण चु० आघूर्ण)

- Both motions of e^- make a combined contribution to the value of magnetic moment of species.

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

S = Sum of spin quantum no. (चक्रण क्वांटम संख्या)

L = Sum of orbital angular momentum q. number (कक्षक कोणीय संवेग क्वांटम संख्या)

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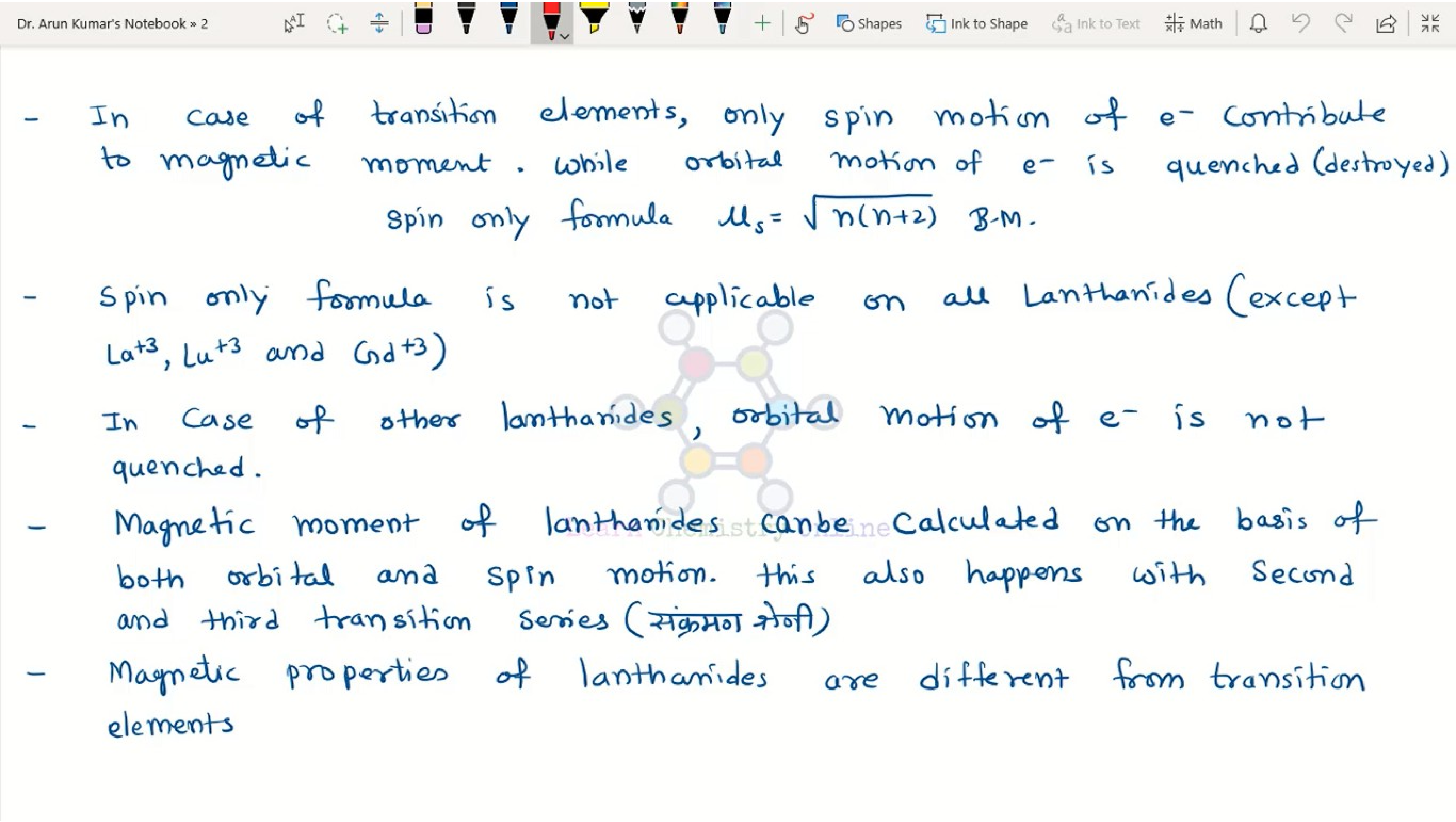

- In case of transition elements, only spin motion of e⁻ contribute to magnetic moment. while orbital motion of e⁻ is quenched (destroyed)

  spin only formula $\mu_s = \sqrt{n(n+2)}$ B.M.

- Spin only formula is not applicable on all Lanthanides (except La^{+3}, Lu^{+3} and Gd^{+3})

- In Case of other lanthanides, orbital motion of e⁻ is not quenched.

- Magnetic moment of lanthanides canbe Calculated on the basis of both orbital and spin motion. this also happens with Second and third transition series (संक्रमण श्रेणी)

- Magnetic properties of lanthanides are different from transition elements

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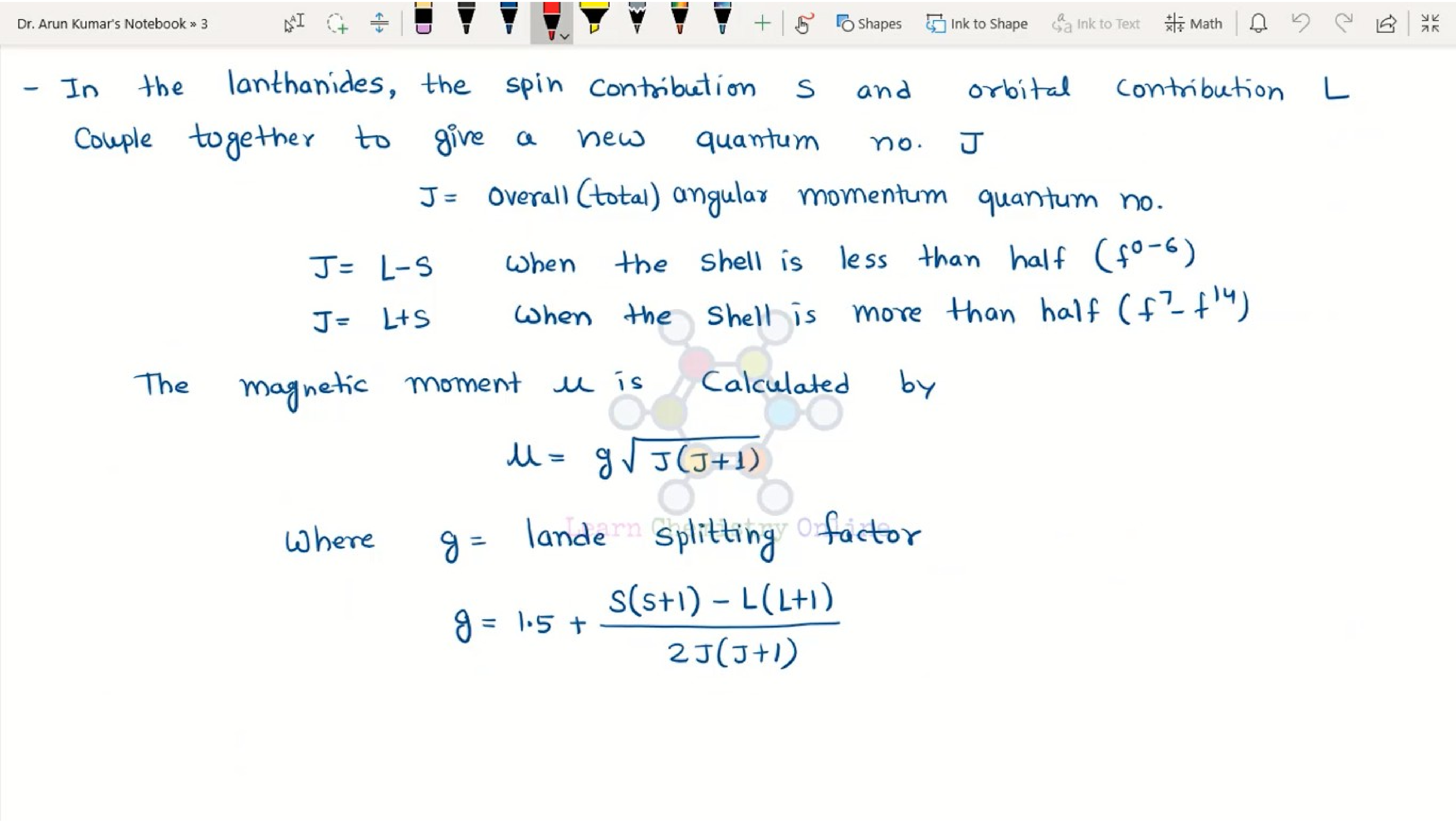

- In the lanthanides, the spin contribution S and orbital contribution L Couple together to give a new quantum no. J

$J =$ Overall (total) angular momentum quantum no.

$J = L - S$ when the shell is less than half (f^{0-6})

$J = L + S$ when the Shell is more than half ($f^{7} - f^{14}$)

The magnetic moment μ is Calculated by

$$\mu = g\sqrt{J(J+1)}$$

Where $g =$ lande Splitting factor

$$g = 1.5 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

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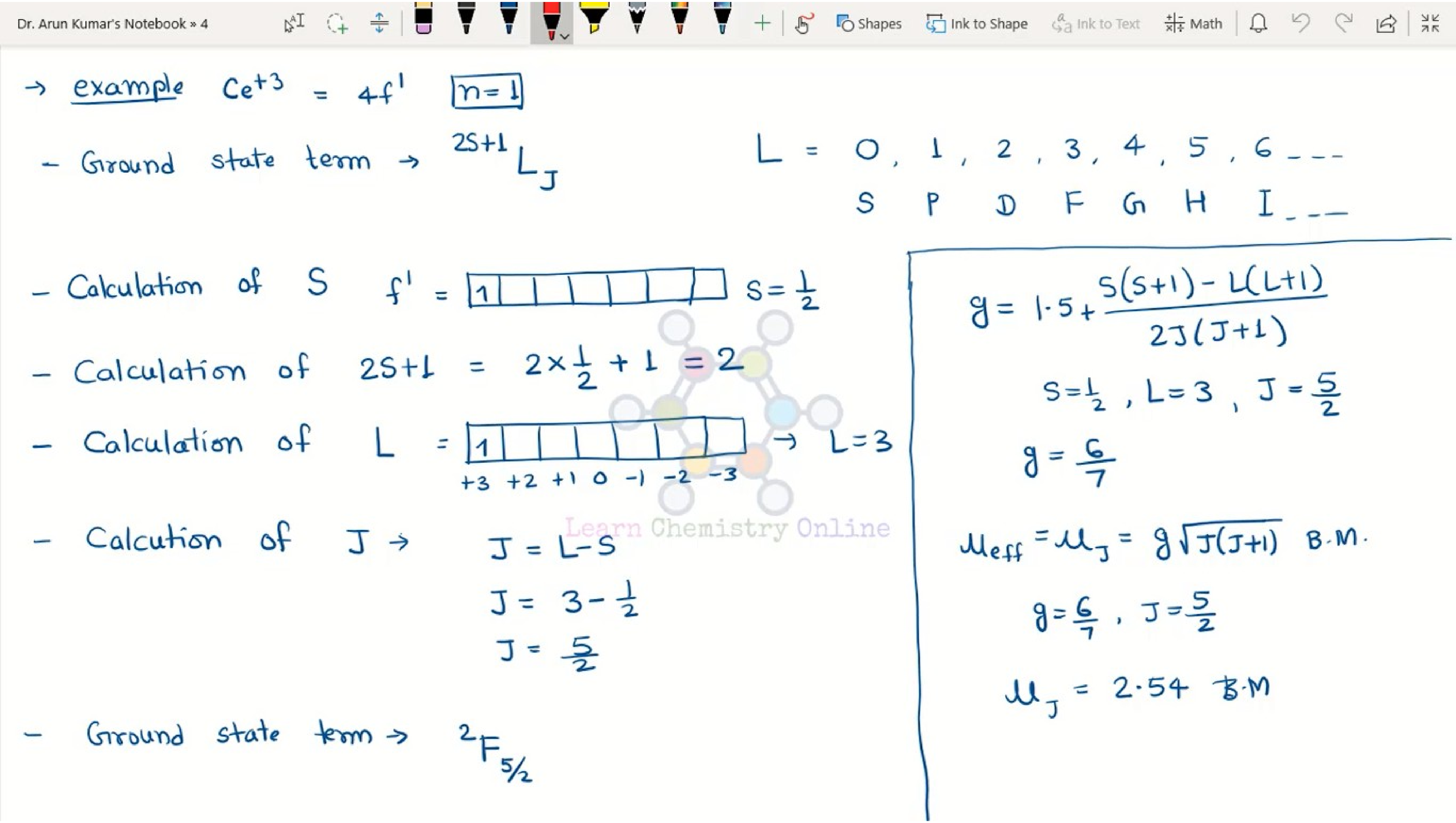

→ example $Ce^{+3} = 4f^1$ $\boxed{n=1}$

- Ground state term → ${}^{2S+1}L_J$

$L = 0, 1, 2, 3, 4, 5, 6 \ldots$

$\quad S \;\; P \;\; D \;\; F \;\; G \;\; H \;\; I \ldots$

- Calculation of S $f^1 = \begin{array}{|c|c|c|c|c|c|c|} \hline 1 & & & & & & \\ \hline \end{array}$ $S = \frac{1}{2}$

- Calculation of $2S+1 = 2 \times \frac{1}{2} + 1 = 2$

- Calculation of $L = \begin{array}{|c|c|c|c|c|c|c|} \hline 1 & & & & & & \\ \hline +3 & +2 & +1 & 0 & -1 & -2 & -3 \end{array} \rightarrow L = 3$

- Calcution of J → $J = L - S$

$J = 3 - \frac{1}{2}$

$J = \frac{5}{2}$

- Ground state term → ${}^2F_{5/2}$

$$g = 1.5 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$S = \frac{1}{2}, L = 3, J = \frac{5}{2}$

$g = \frac{6}{7}$

$\mu_{eff} = \mu_J = g\sqrt{J(J+1)}$ B.M.

$g = \frac{6}{7}, J = \frac{5}{2}$

$\mu_J = 2.54$ B.M

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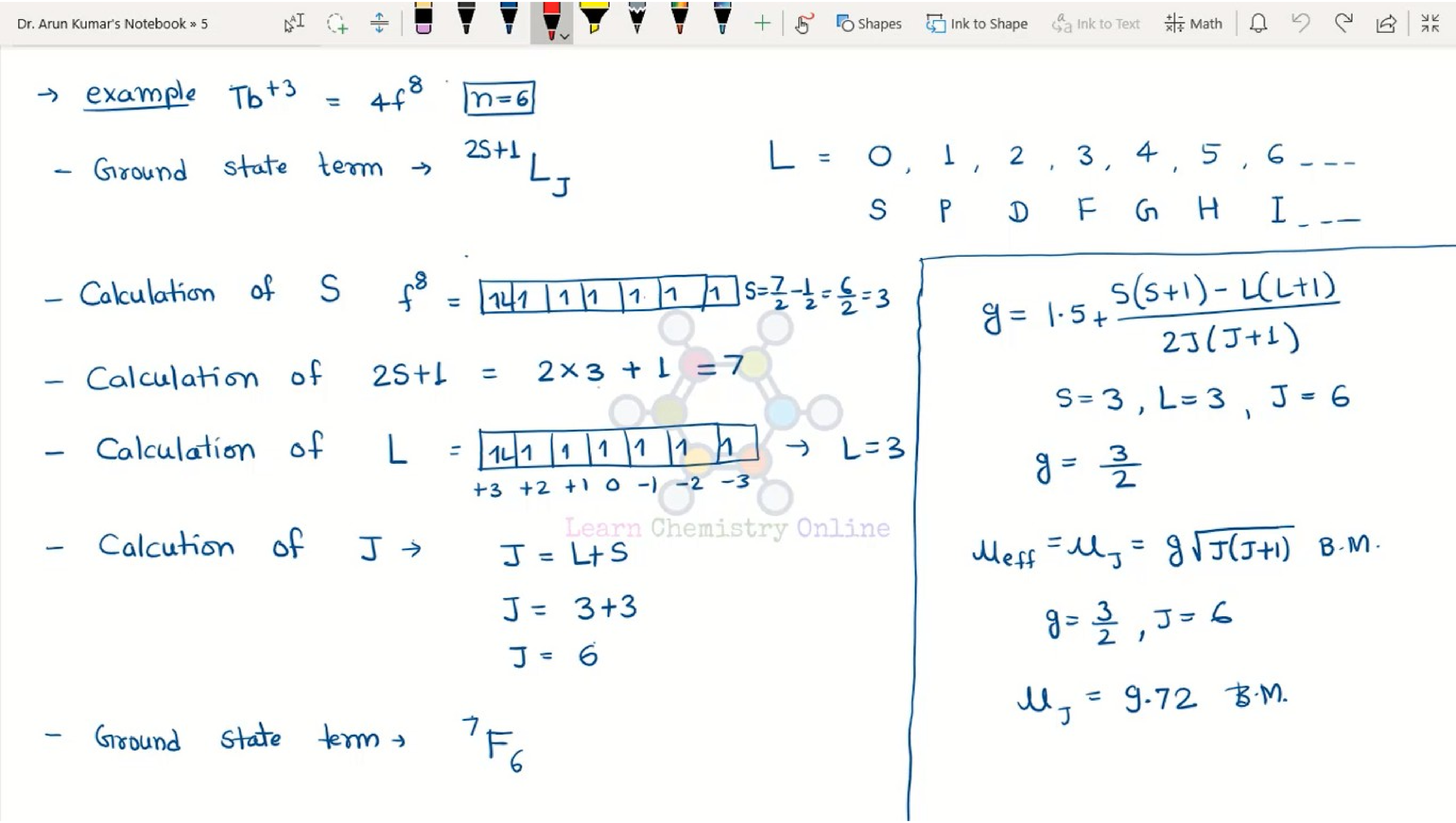

→ example $Tb^{+3} = 4f^8$ $\boxed{n=6}$

- Ground state term → $^{2S+1}L_J$

$L = 0, 1, 2, 3, 4, 5, 6$ ---

S P D F G H I ---

- Calculation of S $f^8 = \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $S = \frac{7}{2} - \frac{1}{2} = \frac{6}{2} = 3$

- Calculation of $2S+1 = 2 \times 3 + 1 = 7$

- Calculation of $L = \underset{+3}{\boxed{\uparrow\downarrow}}\underset{+2}{\boxed{\uparrow}}\underset{+1}{\boxed{\uparrow}}\underset{0}{\boxed{\uparrow}}\underset{-1}{\boxed{\uparrow}}\underset{-2}{\boxed{\uparrow}}\underset{-3}{\boxed{\uparrow}} \rightarrow L = 3$

- Calcution of J → $J = L + S$

$J = 3 + 3$

$J = 6$

- Ground state term → $^7F_6$

$$g = 1.5 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$S = 3, L = 3, J = 6$

$$g = \frac{3}{2}$$

$\mu_{eff} = \mu_J = g\sqrt{J(J+1)}$ B.M.

$g = \frac{3}{2}, J = 6$

$\mu_J = 9.72$ B.M.

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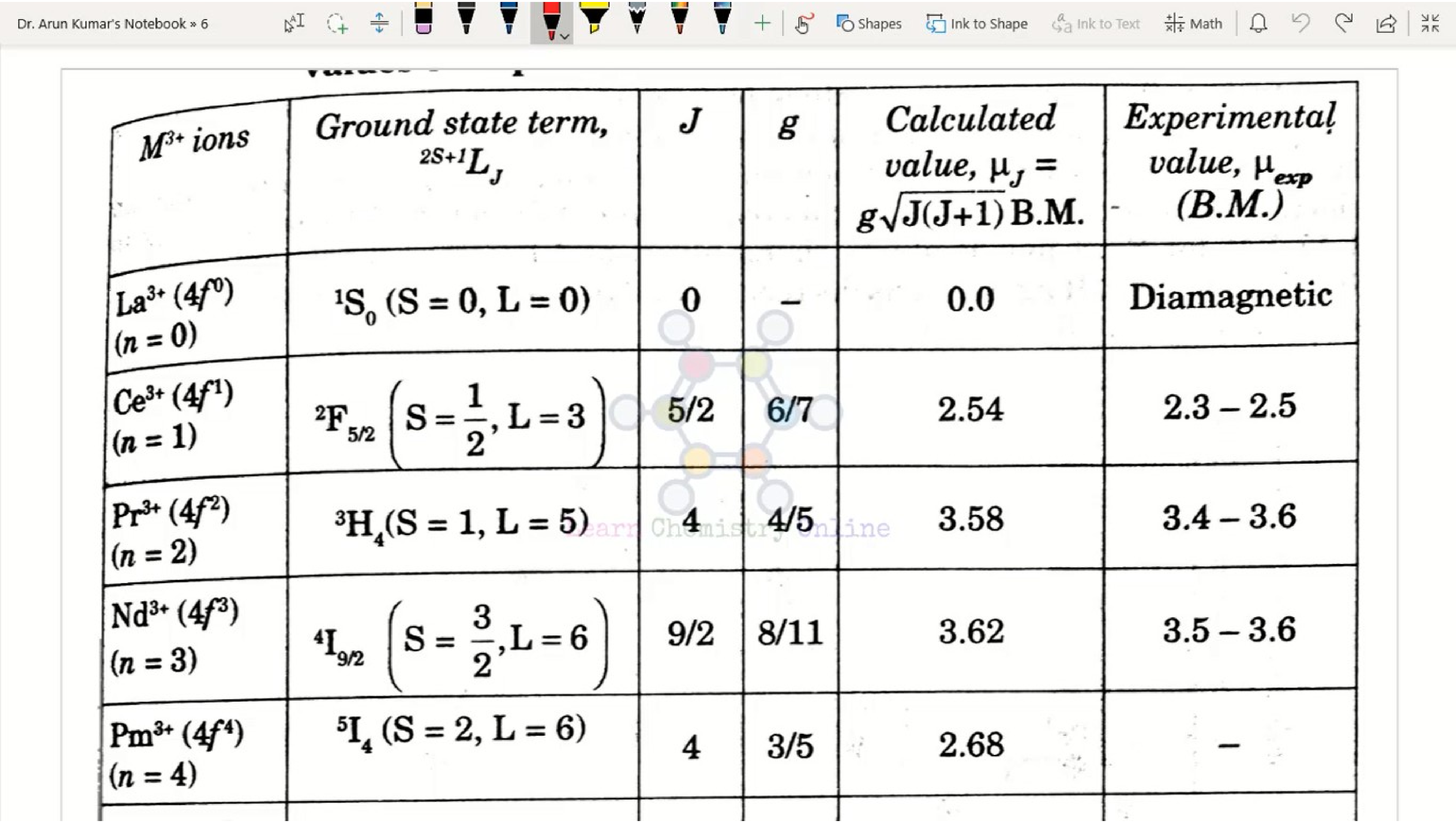

M^{3+} ions	Ground state term, $^{2S+1}L_J$	J	g	Calculated value, $\mu_J = g\sqrt{J(J+1)}$ B.M.	Experimental value, μ_{exp} (B.M.)
La^{3+} ($4f^0$) ($n = 0$)	$^1S_0$ (S = 0, L = 0)	0	–	0.0	Diamagnetic
Ce^{3+} ($4f^1$) ($n = 1$)	$^2F_{5/2}$ $\left(S = \frac{1}{2}, L = 3\right)$	5/2	6/7	2.54	2.3 – 2.5
Pr^{3+} ($4f^2$) ($n = 2$)	$^3H_4$(S = 1, L = 5)	4	4/5	3.58	3.4 – 3.6
Nd^{3+} ($4f^3$) ($n = 3$)	$^4I_{9/2}$ $\left(S = \frac{3}{2}, L = 6\right)$	9/2	8/11	3.62	3.5 – 3.6
Pm^{3+} ($4f^4$) ($n = 4$)	$^5I_4$ (S = 2, L = 6)	4	3/5	2.68	–

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Pm^{3+} ($4f^4$) ($n = 4$)	$^5I_4$ (S = 2, L = 6)	4	3/5	2.68	–
Sm^{3+} ($4f^5$) ($n = 5$)	$^6H_{5/2}$ $\left(S = \frac{5}{2}, L = 5\right)$	5/2	2/7	0.86	1.5 – 1.6
Eu^{3+} ($4f^6$) ($n = 6$)	$^7F_0$ (S = 3, L = 3)	0	–	0.0	3.4 – 3.6
Gd^{3+} ($4f^7$) ($n = 7$)	$^8S_{7/2}$ $\left(S = \frac{7}{2}, L = 0\right)$	7/2	2	7.94	7.8 – 8.0
Tb^{3+} ($4f^8$) ($n = 6$)	$^7F_6$ (S = 3, L = 3)	6	3/2	9.72	9.4 – 9.6
Dy^{3+} ($4f^9$) ($n = 5$)	$^6H_{15/2}$ $\left(S = \frac{5}{2}, L = 5\right)$	15/2	4/3	10.63	10.4 – 10.5
Ho^{3+} ($4f^{10}$) ($n = 4$)	$^5I_8$ (S = 2, L = 6)	8	5/4	10.6	10.3 – 10.5
Er^{3+} ($4f^{11}$)					

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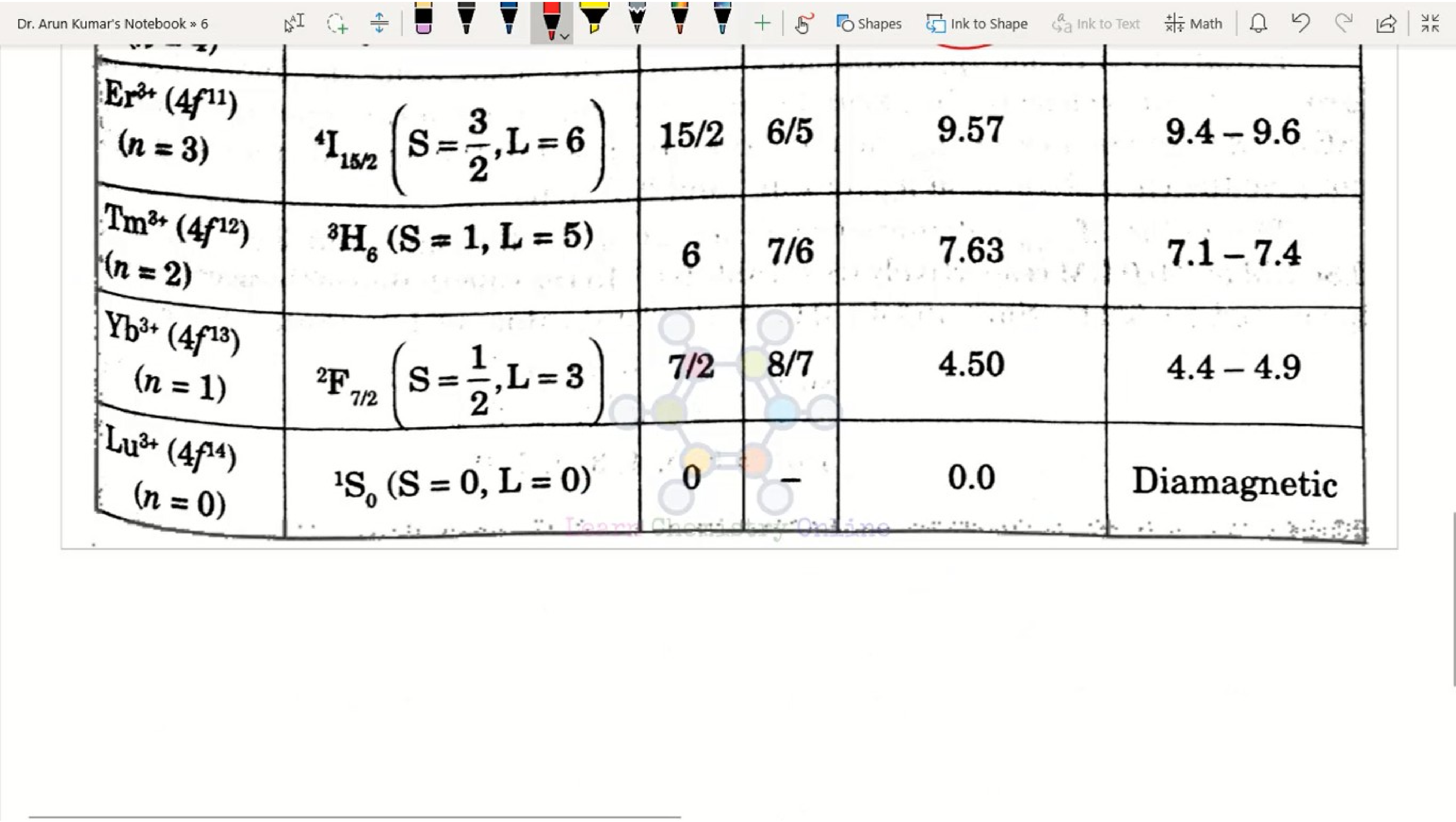

Er^{3+} ($4f^{11}$) ($n = 3$)	$^4I_{15/2}$ $\left(S = \frac{3}{2}, L = 6\right)$	15/2	6/5	9.57	9.4 – 9.6
Tm^{3+} ($4f^{12}$) ($n = 2$)	$^3H_6$ ($S = 1, L = 5$)	6	7/6	7.63	7.1 – 7.4
Yb^{3+} ($4f^{13}$) ($n = 1$)	$^2F_{7/2}$ $\left(S = \frac{1}{2}, L = 3\right)$	7/2	8/7	4.50	4.4 – 4.9
Lu^{3+} ($4f^{14}$) ($n = 0$)	$^1S_0$ ($S = 0, L = 0$)	0	–	0.0	Diamagnetic

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→ Occurrence and isolation of Lanthanides:→

- The source of Lanthanides are unlimited. Each lanthanide mineral contains all lanthanides, although some in traces only, excepting Pm which is an unstable radioactive element.
- Major lanthanide minerals are:-

(i) Monazite (ii) Bastnaesite (iii) Cerite

- Classification of Rare-earth elements:→

- divided into two classes -

ⓐ Cerium group minerals:→

- These are also called cerite-earth minerals or cerium earth minerals.
- This group of mineral contains elements of atomic number from 57 to 63 ($_{57}La$ to $_{63}Eu$).
- These elements are light lanthanides. These are thus light rare earth elements.

② Yttrium group minerals:→

- These are also called yttrium-earth minerals or yttrium earth
- This group of mineral contains elements of atomic number from 64 to 71 ($_{64}Gd$ to $_{71}Lu$).
- These elements are heavier lanthanides. These are thus heavy rare earth elements.

Besides rare earth minerals, there are many other sources of lanthanides. such as phosphates, arsenates, molybdate and tungstates of Ca, Sr, Fe and Pb. In some minerals, Sm, Gd and Eu are present in much larger quantities than in rare earth minerals.

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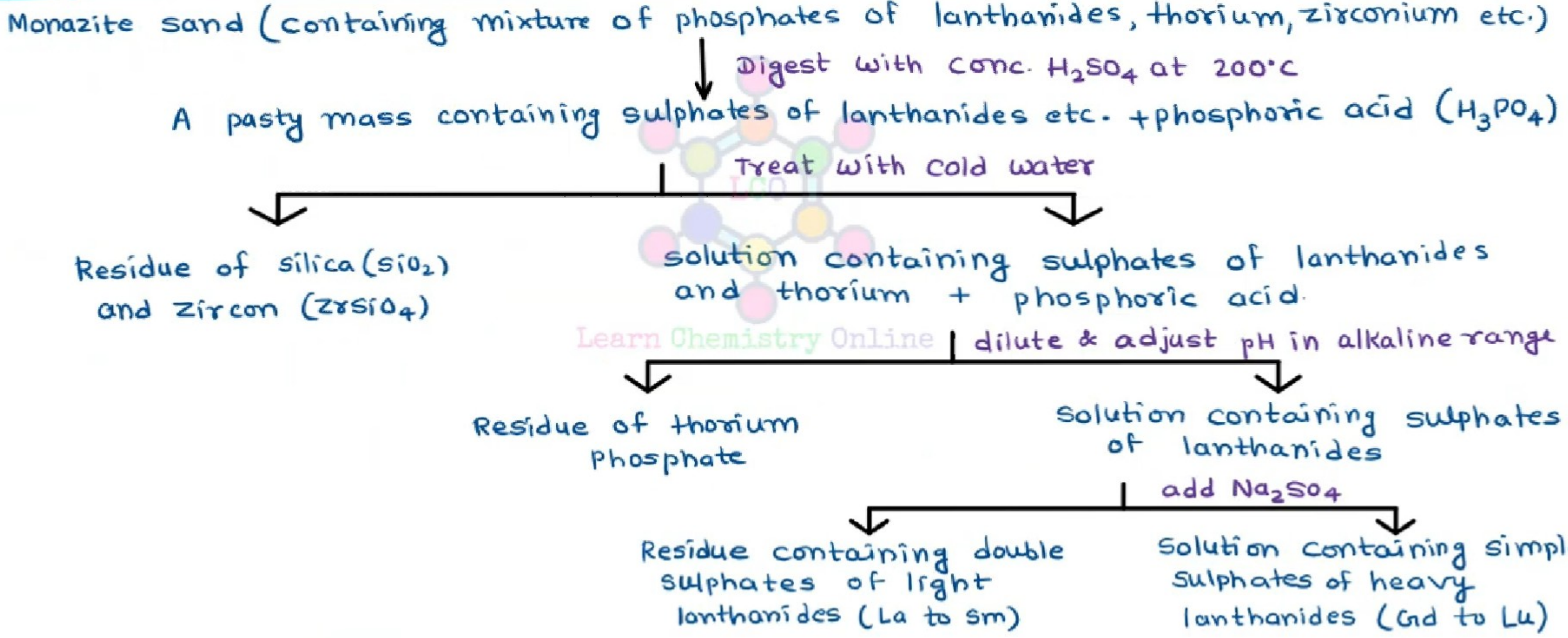
→ Extraction of Lanthanides from Monazite :→

- Extraction of Lanthanides consists of two steps

① To get a mixture of Lanthanides from Monazite

② Separation of lanthanide mixture obtained at step ①

① To get a mixture of Lanthanides from Monazite :→



Monazite sand (containing mixture of phosphates of lanthanides, thorium, zirconium etc.)

↓ Digest with conc. H_2SO_4 at 200°C

A pasty mass containing sulphates of lanthanides etc. + phosphoric acid (H_3PO_4)

Treat with cold water

Residue of silica (SiO_2) and Zircon ($ZrSiO_4$)

solution containing sulphates of lanthanides and thorium + phosphoric acid.

dilute & adjust pH in alkaline range

Residue of thorium Phosphate

Solution containing sulphates of lanthanides

add Na_2SO_4

Residue containing double sulphates of light lanthanides (La to Sm)

Solution containing simple sulphates of heavy lanthanides (Gd to Lu)

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② Separation of Lanthanides from Lanthanide mixture :→

- All the lanthanide elements form M^{+3} ions which are almost identical in size. The chemical properties of these M^{+3} ions are almost the same.
- Due to similar chemical properties, it is difficult to separate the lanthanides from each other. However following methods have been used to separate them.

ⓐ Repeated fractional crystallisation method :→

- Since the solubility of simple salts and double salts of lanthanides decreases from La to Lu, so these lanthanides can be separated from each other by repeating fractional crystalisation of number of times.

ⓑ Fractional precipitation method :→

- when NaOH is added to lanthanide nitrate, hydroxides of lanthanides are formed. $Lu(OH)_3$ is the weakest base and has lower solubility and hence precipited first. while $La(OH)_3$ is the strongest base and higher solubility and hence remains dissolved and precipitate out last of all.

ⓒ Change in oxidation state method :→

- change in oxidation state of lanthanide ion can change their chemical properties. So it is easy to separate lanthanide elements. All lanthanides show +3 oxidation state. the change in oxidation state i.e +2 or +4 can change properties of elements.

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ⓓ Ion-exchange method:→

- This is the most rapid and the most effective method.
- In this method aqueous solution Lathanide tripositive ion is passed through cation exchange resin (HR) and M^{+3} ions replace H^+ ion of the resin and thus get fixed on it.

$$M^{+3}(aq.) + \underset{\text{Solid Resin}}{3HR} \longrightarrow MR_3 + 3H^+(aq.)$$

- In order to recover M^{+3} ions fixed on the resin. MR_3 is treated with citric acid-ammonia citrate solution

$$MR_3 + 3NH_4^+ \longrightarrow 3NH_4R + M^{+3}$$

$$M^{+3} + \text{Citrate ion} \longrightarrow \text{M- citrate complex}$$

- La^{+3} is attached with resin strongly so La-citrate complex comes out last and Lu^{+3} is attached with resin weakly so Lu-citrate complex comes out first.

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ⓔ Solvent extraction method:→

- In this method, two lanthanide compounds are separated from each other on the basis value of partition coefficient of these compounds between two solvents. e.g. separation of $Gd(NO_3)_3$ and $La(NO_3)_3$ using water and tributyl phosphate in kerosene.

ⓕ Fractional decomposition of oxy salts:→ The oxy salts (oxalate, nitrate etc.) decompose on heating and give oxides. The decomposition temp. is different for all oxy salts of lanthanides. Thus different oxides of lanthanides can be obtained by heating at different temp.

(g) complex formation tendency :→

- The stability of complexes of different lanthanide ions is different. due to differnce in stability of complex ion of a given type, the rate and extent of particular reactions are also different. This fact has been used in the separation of lanthanides.

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→ Compounds of Lanthanides:→

① Compounds of Lanthanides in +2 oxidation state:→

- Sm^{+2}, Eu^{+2} and Yb^{+2} form stable compound in aqueous medium.
- The most stable divalent lanthanide is Eu^{+2}. This is stable in water but the solution is strongly reducing.
- $\overset{+2}{Eu}SO_4$ can be prepared by electrolysing $\overset{+3}{Eu_2}(SO_4)_3$ solution.
- $Eu^{+2}Cl_2$ can be made as solid by reducing $Eu^{+3}Cl_3$ with H_2.

$$2EuCl_3 + H_2 \longrightarrow 2EuCl_2 + 2HCl$$

- Aq. Eu^{+3} solutions can be reduced by Mg, Zn, zinc amalgam or electrolytically to give Eu^{+2}.
- EuH_2 is ionic and similar to CaH_2. Eu^{+2} is resembles Ca^{+2} is several ways. i.e. solubilities in water, strong HCl and in liquid NH_3. but their magnetic properties are different. Eu^{+2} is paramagnetic whereas Ca^{+2} is diamagnetic.
- The couple $Eu^{+3} | Eu^{+2}$ has a standard reduction potential of −0.41 Volts. So this act as strong reducing reagent and do not reduce water.
- Yb^{+2} and Sm^{+2} can be prepared by electrolytic reduction of their trivalent ions in aqueous solution. However, the Ln^{+2} ions are readily oxidised by air. These two elements form hydroxides, carbonates, halides, sulphates and phosphates.

- The Nd^{+2}, Pm^{+2}, Sm^{+2} and Gd^{+2} are only found in solid dihalides $LnCl_2$ and LnI_2. These dihalides can be made by reducing the trihalides with hydrogen or metal or with sodium amalgam. These dihalides show metallic conduction.
- The stability of some Ln^{+2} ions is due to half filled and completely filled sub-shells.

② Compounds of Lanthanides in +3 oxidation state :→

- The metals are all soft and silvery white. They are electropositive and highly reactive.
- The heavier metals are less reactive than the lighter ones because they form a layer of oxide on the surface.
- The chemical properties of the group are essentially the properties of trivalent ionic compounds.
- The sum of first three ionisation energies varies from La^{+3} to Lu^{+3}. which is associated with empty, half filled and full filled f subshell.
- The standard electrode potential are all high (−2.48 to −2.26 V). The lanthanides are much more reactive than Al ($E^\circ = -1.61$ V) and slightly more reactive than Mg ($E^\circ = -2.37$ V). Thus they react slowly with cold water, but more rapidly on heating.

$$2Ln + 6H_2O \longrightarrow 2Ln(OH)_3 + 3H_2$$

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- The hydroxides $Ln(OH)_3$ are precipited as gelatinous precipitate by the addition of NH_4OH to aqueous solutions.
- These hydroxides are ionic and basic. They are less basic than $Ca(OH)_2$ but more basic than $Al(OH)_3$. The basicity decreases as the ionic radius decreases from Ce to Lu. Thus $Ce(OH)_3$ is the more basic and $Lu(OH)_3$ is the least basic.
- The metals becomes dull when reacts with air due to formation of oxide. On heating in O_2, they all give oxides LnO_3. Yb and Lu form a protective oxide film, which prevents the bulk of the metal forming the oxide unless it is heated to 1000°C. The exception is Ce, which forms CeO_2 rathe than Ce_2O_3. The oxides are ionic and basic. Basic strength decreases as the ion get smaller.
- The metal reacts with H_2 at 300-400°C and forms LnH_2. Eu and Yb have tendency to form EuH_2 and YbH_2 and are salt-like hydrides and contain M^{+2} and $2H^-$. The other all form hydrides LnH_2 which are black, metallic and conduct electricity. These are better formulated as Ln^{+3}, $2H^-$ and an electron which occupies a conduction band.

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- The hydrides are stable to heat up to 900°c. They are decomposed by water, and react with oxygen.

$$CeH_2 + 2H_2O \longrightarrow CeO_2 + 2H_2$$

- These dihydrides take up H if heated under pressure and all except Eu form salt-like hydrides LnH_3 made up of Ln^{+3} and three H^-. These do not have a delocalised electron, and do not show metallic conduction.
- The anhydrous halides MX_3 can be made by heating the metal and halogen or by heating the oxide with ammonium halide.

$$Ln_2O_3 + 6NH_4Cl \xrightarrow{300^\circ c} 2LnCl_3 + 6NH_3 + 3H_2O$$

- The fluorides are very insoluble and can be precipited from solutions of Ln^{+3} by addition of NaF or HF. This is used as a test for the lanthanides in qualitative analysis. However with excess F^-, the smaller lanthanide ions may form soluble complex $[LnF(H_2O)_n]^{2+}$.
- The chlorides are deliquescent and soluble and crystallise with six or seven H_2O molecules. If the hydrated halides are heated they form oxohalides instead of dehydrating to give anhydrous halides.

$$LnCl_3 \cdot 6H_2O \xrightarrow{\Delta} LnOCl + 5H_2O + 2HCl$$

- On heating $CeX_3 \cdot (H_2O)_n$, it gives CeO.
- The bromides and iodies are similar to the chlorides.
- At high temp, the lanthanides reat with B to give LnB_4 and LnB_6.
- On heating metal with C in inert atomosphere they form LnC_2 and $Ln_4(C_2)_3$. The carbides are also formed by reducing Ln_2O_3 with C in an electric furnace.
- The LnC_2 are more reactive than CaC_2. They react with water to give ethyne and hydrogen. They also show metallic conductivity. They not contain Ln^{+2} and are best described as Ln^{+3} and C_2^{2-} with an extra electron in a conduction band.

$$2LnC_2 + 6H_2O \longrightarrow 2Ln(OH)_3 + 2C_2H_2 + H_2$$

$$C_2H_2 + H_2 \longrightarrow C_2H_4 + H_2 \longrightarrow C_2H_6$$

- At higher temp the metals also react with N, P, As, Sb and Bi to give LnN and other compounds. the LnN reacts with water to give hydroxide.

$$LnN + 3H_2O \longrightarrow Ln(OH)_3 + NH_3$$

- These metal ions also form nitrates, carbonates, oxalates, sulphates, perchlorates etc.

③ Compounds of Lanthanides in +4 oxidation state:→

- The only +4 lanthanide ion is Ce^{+4}. which is exist in aqueous solution.
- The Ce^{+4} is heavily hydrated due to its high charge.
- The Ce^{+4} solutions are used as an oxidising agent in volumetric analysis instead of $KMnO_4$ or $K_2Cr_2O_7$.
- The aqueos Ce^{+4} solutions can be prepared by oxidising a Ce^{+3} solution with a very oxidising agent such as ammonium peroxodisulphate $(NH_4)_2S_2O_8$.
- The Ce^{+4} is also used in organic reactions. for example oxidation of alcohol, aldehyde and Ketones at α-carbon.
- CeO_2 (white) can be obtained by heating the metal or $Ce(OH)_3$ or $Ce_2(C_2O_4)_3$ in air. CeO_2 is a fluorite type structure. It is insoluble in acids and alkali but dissolved if reduced to Ce^{+3}.
- $Ce(SO_4)_2$ is well known and is yellow like $K_2Cr_2O_4$.
- CeF_4 (white) is obtained by CeF_3 and F_2.
- Ce^{+4} also forms various stable complexes such as $(NH_4)_2[Ce(NO_3)_6]$ etc.
- The other Ce^{+4} compounds are oxides, fluorides and fluoro complexes but unstable in water.
- The elements Pr, Nd, Tb and Dy also forms +4 states. These are unstable, and occur only as solid. They also form nonstoichiometric oxides and fluorides.

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