UNIT II

STRUCTURE AND BONDING   II

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INTRODUCTION

* The binary compounds of boron and hydrogen are called boranes.
* They are electron deficient and good reducing agents.

BORANES

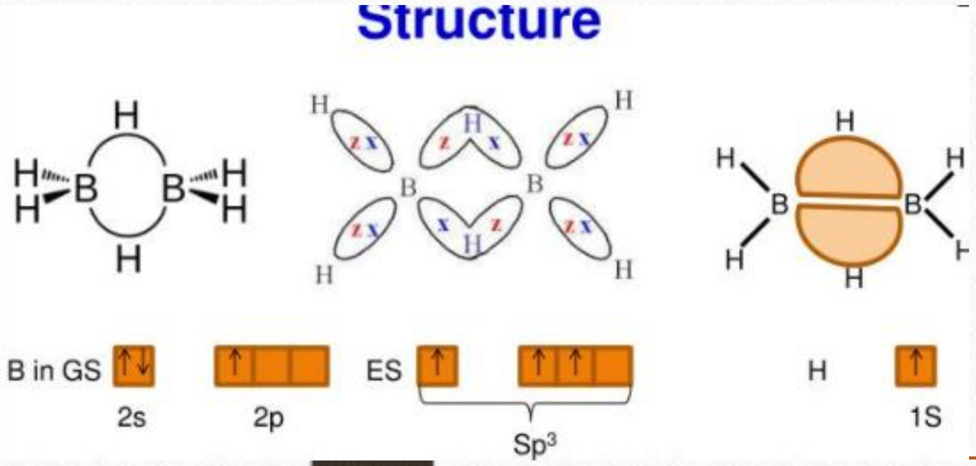
* The parent member BH_3 is called boranes, it dimerises to form diborane B_2H_6
* The general formula of borane is BxHy
* The most important boranes are diborane pentaboranes B_5H_9 and decaborane $B_{10}H_{14}$
* Boranes are all colourless and diamagnetic
* Boranes are highly reactive

BH3 borane (3)
B2H6 diborane (6)
B3H7 triborane (7)
B4H10 tetraborane (10)

B5H9 pentaborane (9)
B5H11 pentaborane (11).
B6H10 hexaborane (10)
B10H14 decaborane (14)

DIBORANE

* Diborane is simplest boranes.
* It has the less number of valence electron than the number required to form all the electron pair bond in its structure.
* Two hydrogen bridges are present.
* The model determined by MOT indicates that the bond between boron and terminal hydrogen atoms are 2c-2e bond.
* Having used 2 electrons in bonding to terminal hydrogen atoms. Each boron has one valence e-remain for additional bonding.The bridging hydrogen provides an electron each.



❖ BONDING AND STRUCTURE IN DIBORANE

- The diborane molecule has 2 type of bonds.
- 1. four terminal (2c-2e) B-H bonds.
- 2. two bridged (3c-2e) B-H-B bonds.

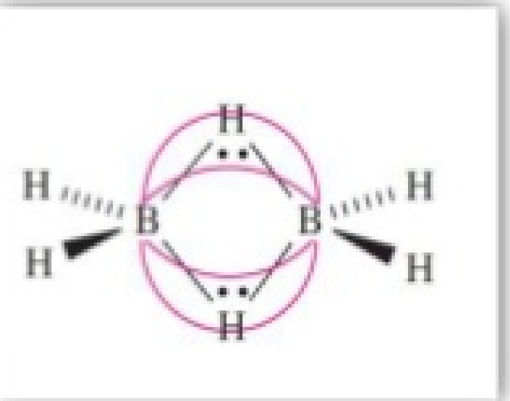
- 1. four terminal (2c-2e) B-H bonds.

  Each of these bonds are formed by sharing of 2 electrons between boron and terminal hydrogen atoms. It's a normal σ covalent bond.

- 2. two bridged (3c-2e) B-H-B bonds.

  Each of these bond is formed by sharing of 2 electrons between 2 B and 1 H atoms .

- It is also called as banana bond

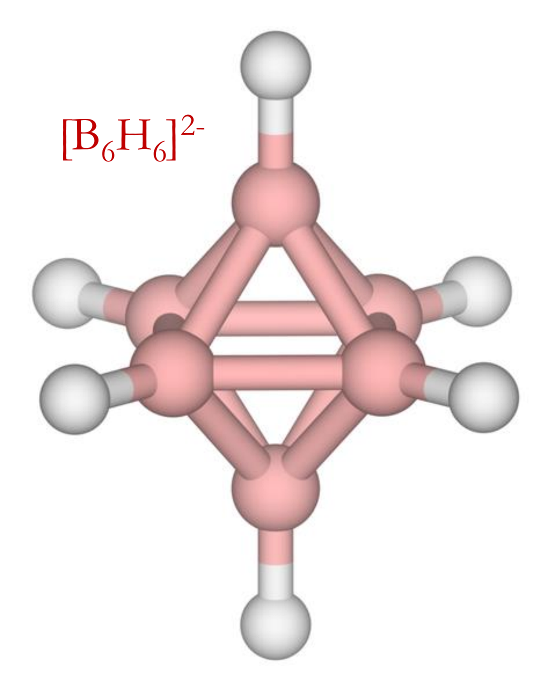


TYPES OF BORANES

* CLOSO * NIDO * ARACHNO

*** closo boranes:**

* closed triangular polyhedral structure.
* All the vertices of the triangular polyhedron are occupied by B atoms.
* General formula: $[B_nH_n]^{2-}$ (e.g.,) $[B_6H_6]^{2-}$
* It has (n+1) skeletal bonding electron pair.
* n is the total number of B atoms.



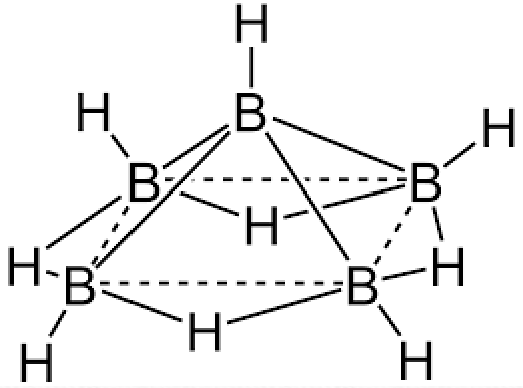
NIDO BORANES

- Nido boranes are formed when one corner of the polyhedral is removed
- nest like non closed structure
- General formula B_nH_{n+4} (e.g.,) B_5H_9, B_2H_6

ARACHNO BORANES

- These Boranes are formed when the two corners of polyhedral are removed.
- Web like non closed polyhedral structure.
- General formula B_nH_{n+6}

B_4H_{10}



Pentaborane(9)

Hypo Boranes

* Hypo net like
* These have most open cluster in which Boron atoms occupy n corners of (n+3) polyhedron.
* General formula: B_nH_{n+8}
* These Boranes are having complex structure.
* Example: B_8H_{16} and $B_{10}H_{18}$.

Conjucto Boranes

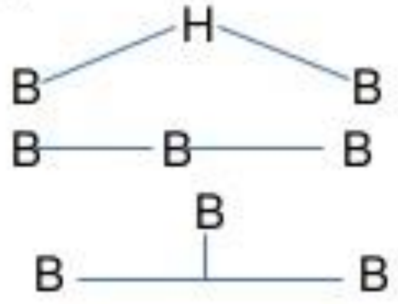
* These Boranes formed by linking of 2 or more of any other type of Boranes.
* These structures are very complex.
* General formula: B_nH_m
* Example: $(B_5H_9)2$,$(B_4H_{10})2$

❖ BONDING IN BORANES

- 2c-2e bond → B· ·H
- 3c-2e bond → B------H.------.B
  → B.------.H------B

❑ In boranes 4 types of bonds are present

1. 3c-2e B-H-B Bent
2. 3c-2e B-B-B Open
   Closed



3. 2c-2e B-B Normal
4. 2c-2e B-H Normal

❖ STYX CODES

The over all boranes bonding can be represented by 4 digital numbers

S = number of B-H-B bonds (1^{st} digit)

T = number of B-B-B bonds (2^{nd} digit)

Y = number of B-B bond (3^{rd} digit)

X = number of $B\text{-}H_2$ groups (4^{th} digit)

Ex: B_2H_6 (Diborane)

S = number of B-H-B bonds = 2

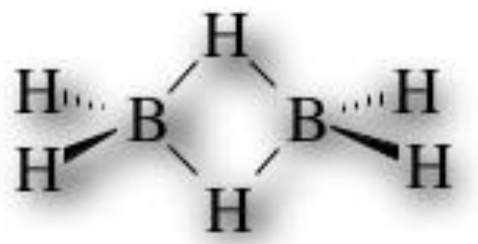
T = number of B-B-B bonds = 0

Y = number of B-B bond = 0

X = number of $B\text{-}H_2$ groups = 2

Hence for diborane styx code is 2002.

Example – B_4H_{10} styx code is 4012



TETRABORANE(10)

It can be clearly seen that there are 4 B-H-B bridges,no closed or bridging B-B-B unit, one B-B bond and two terminal BH2 groups.Hence the overall SYTX code for B4H10 is 4012.

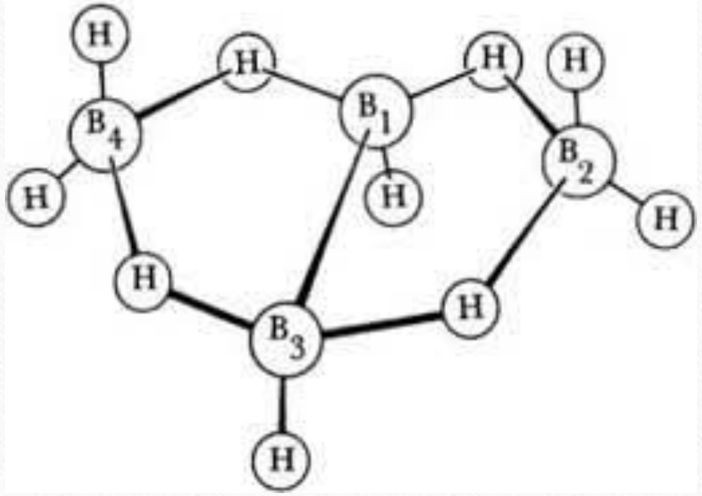


Table 3. Nature and number of bonds (along with electrons required) present in B_4H_{10}.

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 4 B atoms	Contribution from 10 H atoms
B–H–B	4	8	4	4
B–B–B	0	0	0	0
B–B	1	2	2	0
B–H	6	12	6	6

Hence four 3-centre 2-electron and seven 2-centre 2-electron bonds require a total of 4x2+7x2=22 electrons.

Four Boron atoms have 12 valence electrons while 10 electrons are contributed by ten hydrogen groups that participating in both types of bonds.

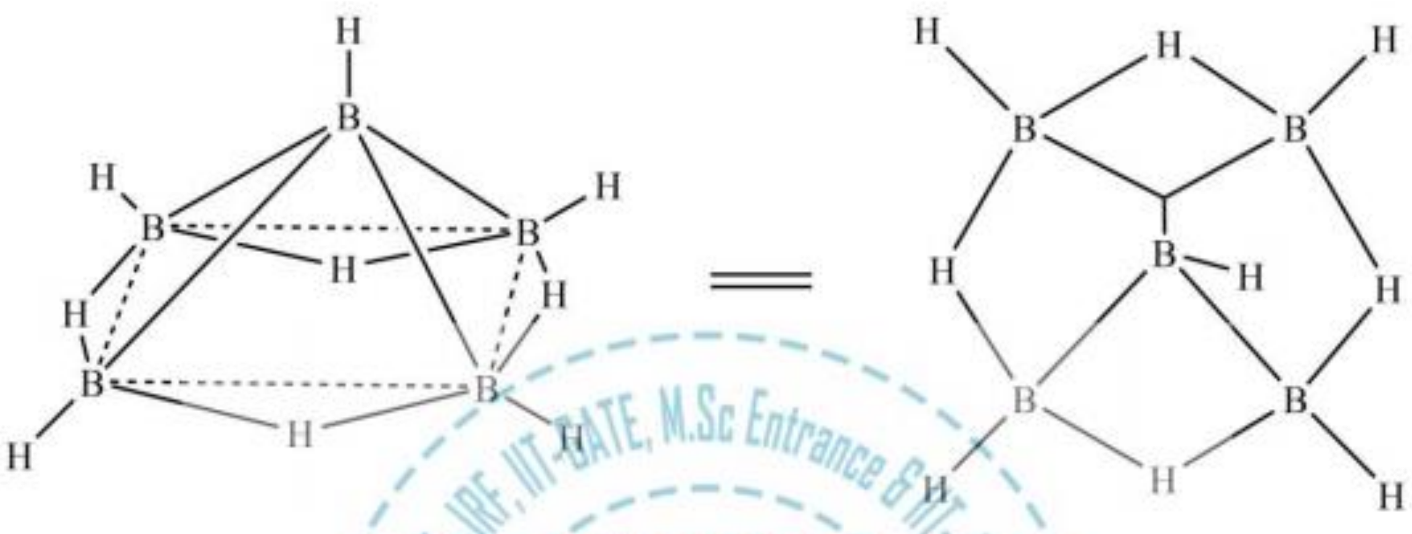


Figure 5. Structure of B_5H_9.

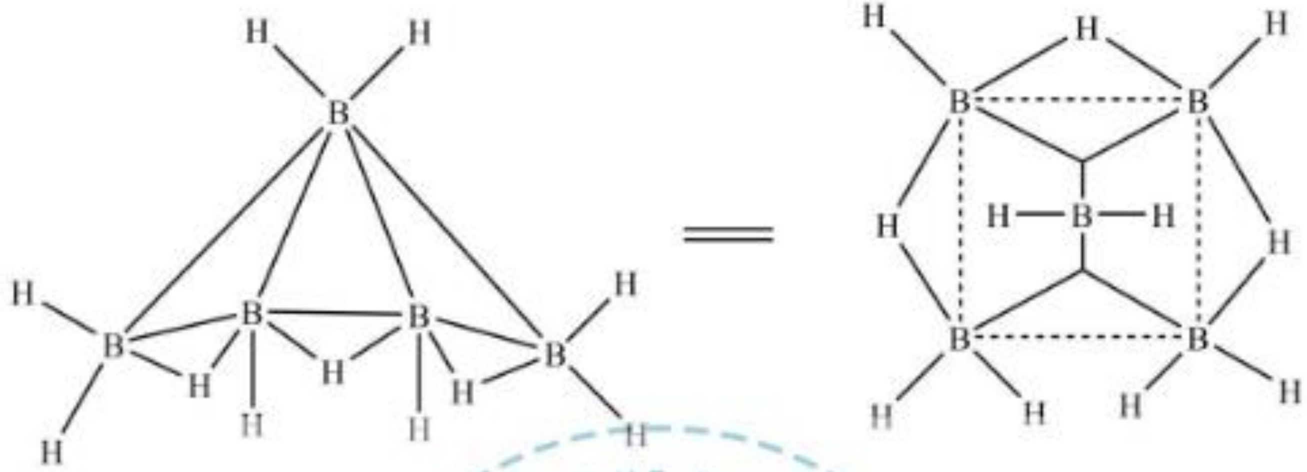
Its structure is that of five atoms of boron arranged in a square pyramid.Each boron has a terminal hydride ligand and four hydrides span the edges of the base of the pyramid.There are four B-H-B bridges,one closed or triply bridged B-B-B unit,two B-B bond and no terminal BH2 groups.Hence SYTX code is 4120.

Table 4. Nature and number of bonds (along with electrons required) present in B_5H_9.

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 5 B atoms	Contribution from 9 H atoms
B–H–B	4	8	4	4
B–B–B	1	2	2	0
B–B	2	4	4	0
B–H	5	10	5	5

Hence five 3-centre 2-electron bond and seven 2centre 2-electron bonds require a total of 5x2+7x2=24 electrons. Five Boron atoms have 15 valence electrons while 9 electrons are actually contributed by 9 hydrogen groups that are participating in both types of bonds

PENTABORANE (11)



The pentaborane -11 is having unsymmetrical square-pyramid and five boron atoms are present at the five corners of a squarepyramid.Three out of five boron atoms have a terminal hydride ligand while two adjacent boron on the base of the pyramid has two hydride groups each, and four hydrides span the edges of the base of the pyramid.

There are three B-H-B bridges,two closed or triply bridged B-B-B bond and three terminal BH2 groups.Hence overall SYTX code is 3203.

Table 5. Nature and number of bonds (along with electrons required) present in B_5H_{11}.

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 5 B atoms	Contribution from 11 H atoms
B–H–B	3	6	3	3
B–B–B	2	4	4	0
B–B	0	0	0	0
B–H	8	16	8	8

Hence five 3-centre 2-electron and eight 2-centre 2-electron bonds require a total 5x2+8x2=26 electrons.Five Boron atoms have 15 valence electrons while 11 electrons are actually contributed by elevan hydrogens actually contributed by elevan hydrogen groups that are participating in both types of bonds.

HEXABORANE(10)

It can be seen that there are four B-H-B bridges, and closed or triply bridged B-B-B unit two B-B bonds and no terminal BH2 groups.Hence the SYTX code is 4220.

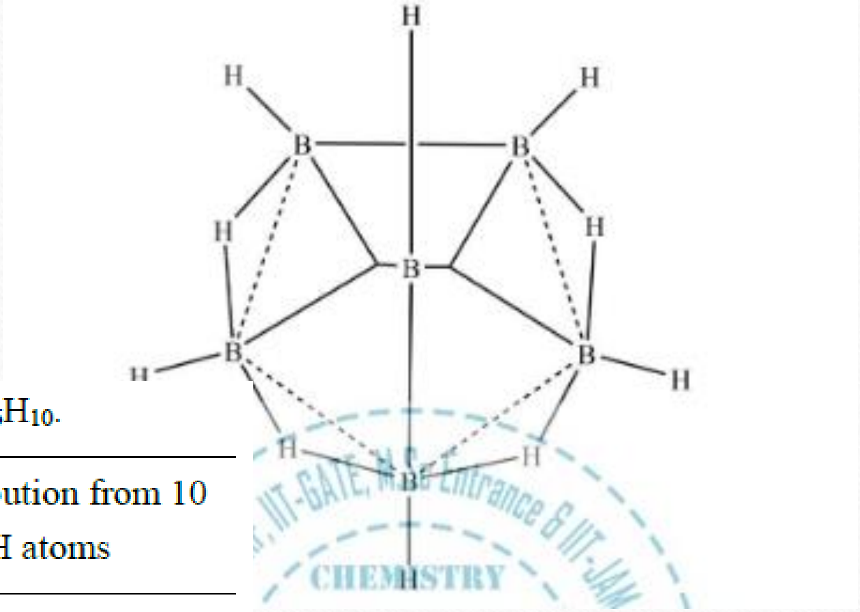


Table 6. Nature and number of bonds (along with electrons required) present in B_6H_{10}.

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 6 B atoms	Contribution from 10 H atoms
B–H–B	4	8	4	4
B–B–B	2	4	4	0
B–B	2	4	4	0
B–H	6	12	6	6

Hence six 3-centre 2-electron and eight 2-centre 2-electron bonds require a total 6x2+8x2=28 electrons.Six boron atoms have 18 valence electrons while 10 electrons are actually contributed by ten hydrogen groups that are participating in both typesof bonds.

DECABORANE(14)

In decaborane, the B10 framework resembles an incomplete octahedron.Each Boron has one radial hydride,and four Boron atoms near the open part of the cluster feature extra hydrides.There are four B-H_B bridges,six B-B-Bunits (four B-B-B triple bridge bonds and two B-B-B bent bridge) two B-B bonds and zero terminal BH2groups.Hence SYTX code is4620.

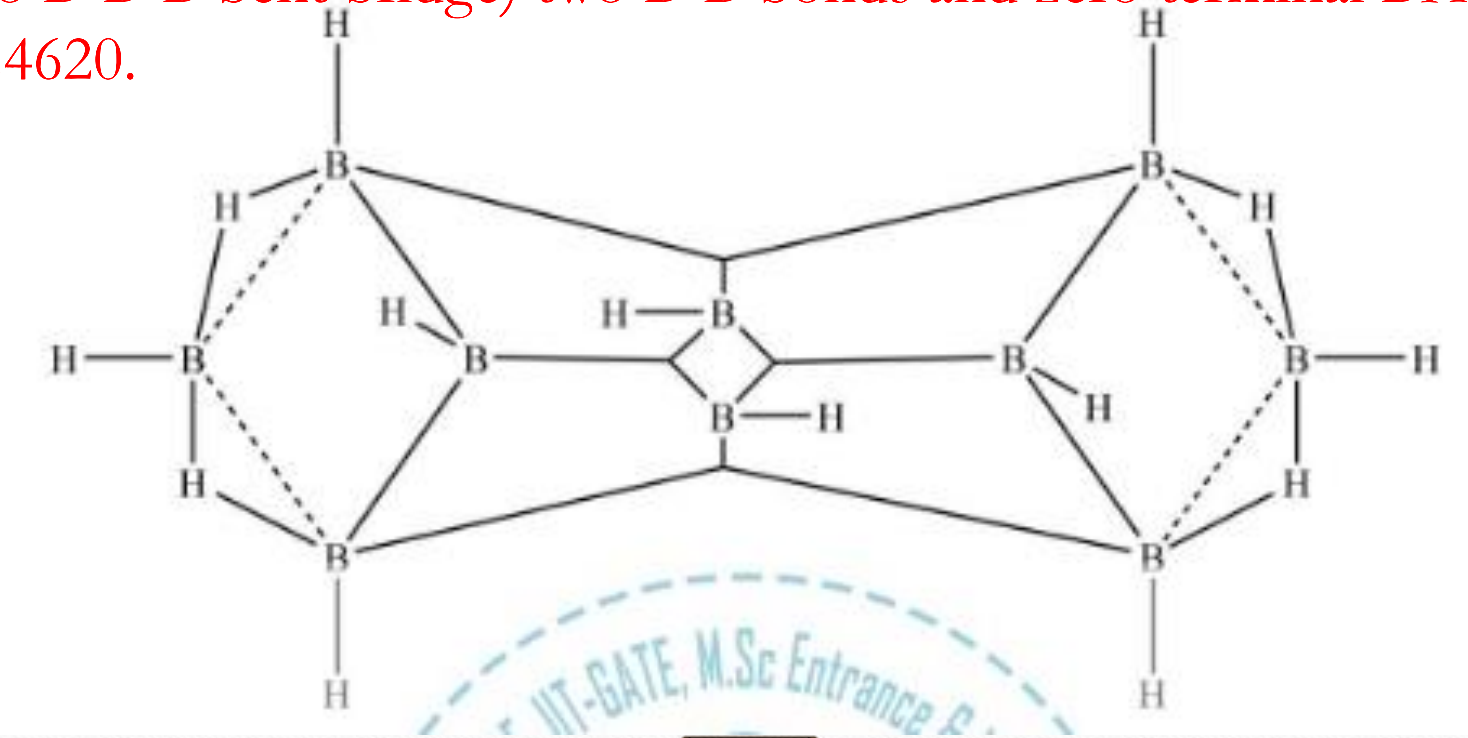


Table 7. Nature and number of bonds (along with electrons required) present in $B_{10}H_{14}$.

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 10 B atoms	Contribution from 14 H atoms
B–H–B	4	8	4	4
B–B–B	6	12	12	0
B–B	2	4	4	0
B–H	10	20	10	10

Hence ten 3-centre 2-electron and twelve 2-centre 2-electron bond require a total 10x2+12x2=44 electrons. Ten Boron atoms have 30 valence electrons while 14 electrons are actually contributed by fourteen hydrogen groups which are participating in both types of bonds.

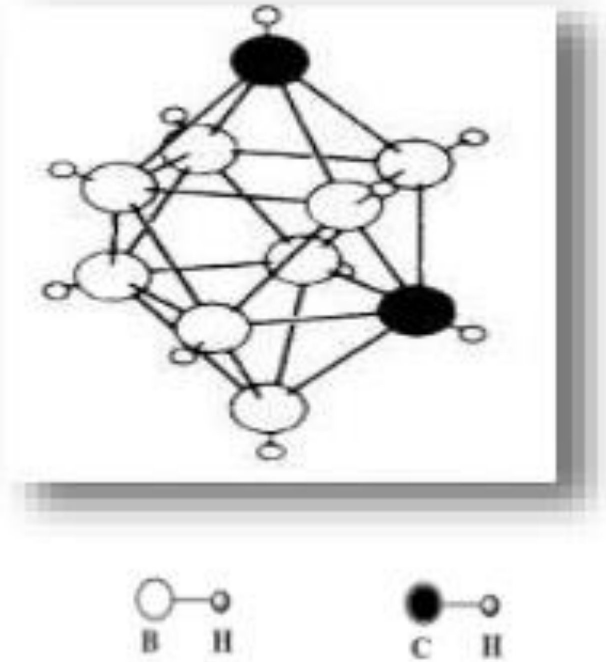
CARBORANES

- Carboranes are mixed hydrides of boron and carbon in which carbon and boron atoms occupy the vertices of triangulated polyhedron.
- Carboranes are most important heteroboranes.
- Carboranes are member of a class of organometallic compounds containing carbon (C), boron (B), and hydrogen (H).
- General formula of carboranes is $C_2B_nH_{n+m}$, where n is an integer
- carboranes with n ranging from 3 to 10 have been characterized.
- Boranes and carboranes have same number of electrons in their bonding framework , will have similar structure.

❖ TYPES OF CARBORANES

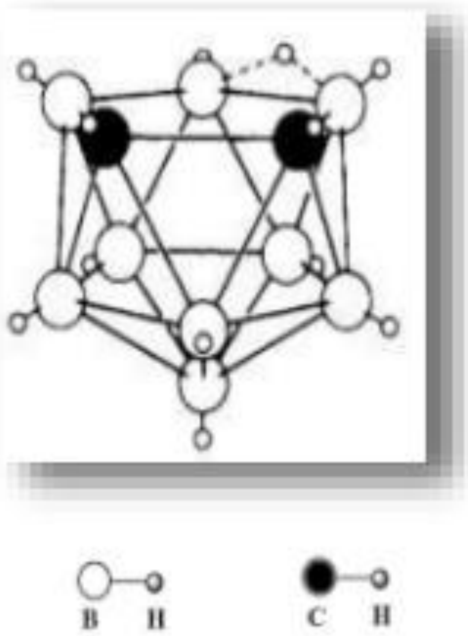
➢ CLOSO CARBORANES

- Closed, triangulated polyhedra structure.
- General formula: $C_2B_nH_{n+2,}$
- Total number of electron in bonding framework is $(2n+2)e^-$. i.e. (n+1) e pairs.
- Example-1,6-$C_2B_8H_{10}$



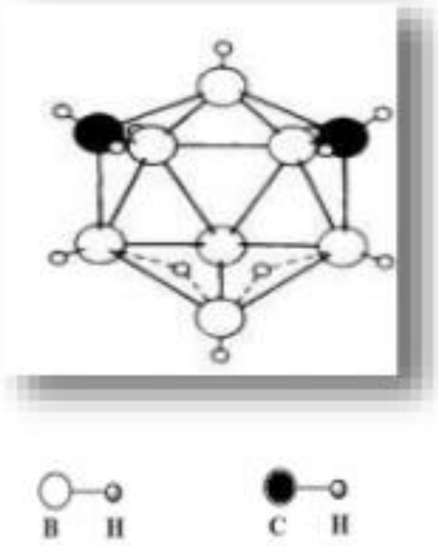
➢ NIDO CARBORANES

- One corner of triangulated polyhedra is removed
- General formula: $C_2B_nH_{n+4,}$
- Total number of electron in bonding framework is $(2n+4)e^-$. i.e. $(n+2)$ e^- pairs.
- Example- $C_2B_4H_8$, $[1,7\text{-}C_2B_9H_{12}]^-$



➢ ARACHNO CARBORANES

- Two corners of triangulated polyhedra is removed.
- General formula: $C_2B_nH_{n+6,}$
- Total number of electron in bonding framework is $(2n+6)e^-$. i.e. $(n+4)$ e^- pairs.
- Example- 1,3-$C_2B_7H_{13}$



❖ WADE'S RULE

In chemistry polyhedral skeletal electron pair theory provides electron containing rules useful for predicting structures of boranes and carboranes. It is formulated by Wade and hence it is called as Wade's rule.

➢In Wade's rule

i. Each BH unit donates $2e^-$ to skeletal structures.

ii. Each CH unit donates $3e^-$.

iii. -ve charge on borane gives an electron.

iv. Additional hydrogen atom gives one electrons each.

Types	Formula	Skeletal Electron Pairs	Example
Closo	B_nH_n	n + 1	$[B_5H_5]^{2-}$
Nido	B_nH_{n+4}	n + 2	B_2H_6
Arachno	B_nH_{n+6}	n + 3	B_4H_{10}
Hypho	B_nH_{n+8}	n + 4	None

The type of structure adopted by a compound is related to the no of electrons that are available for bonding within the polyhedral framework.

K. Wade provided the rules to correlate no of framework electrons with the structure of boron clusters.Later Mingo extended the rules for the transition metal clusters.

No of framework electrons (F) $= TVE - 2n$

No of bonding electron pair (F/2) $= \frac{TVE - 2n}{2}$

$$(F/2) = \frac{3B + 4C + H + x - 2n}{2}$$

B = No of boron atoms

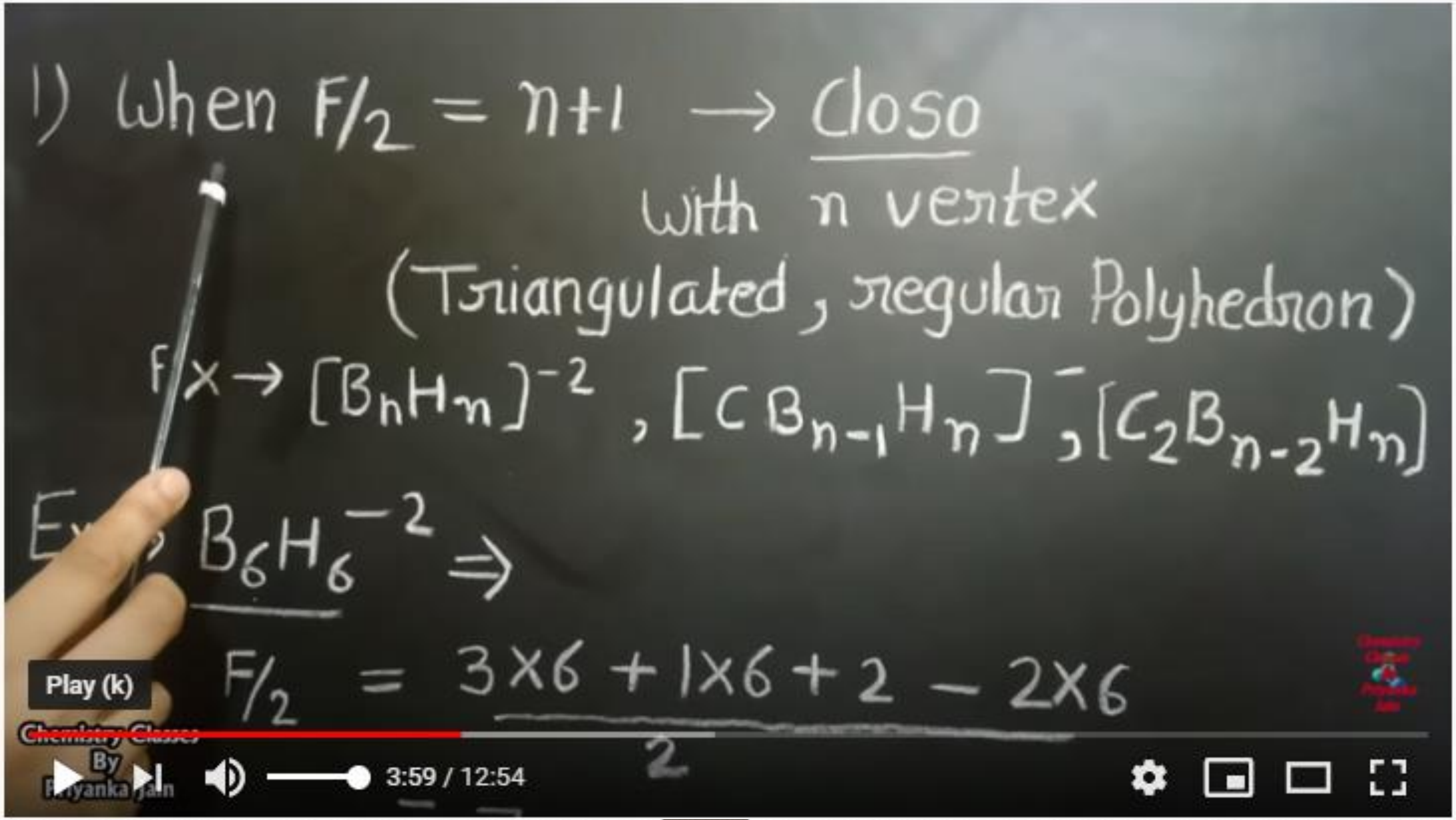
C = No of carbon atoms

H = No of hydrogen atoms

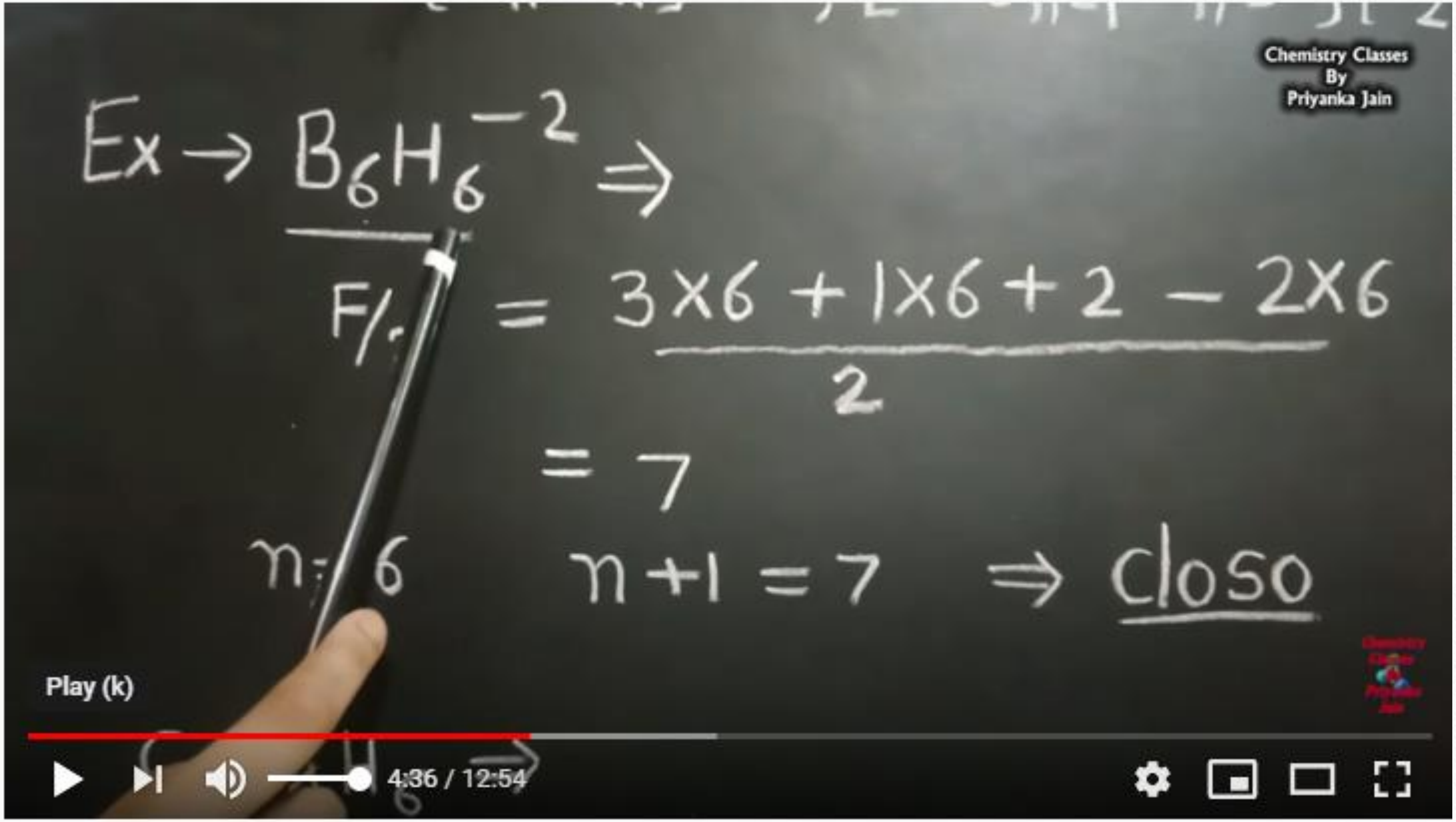
x =Amount of negative charges

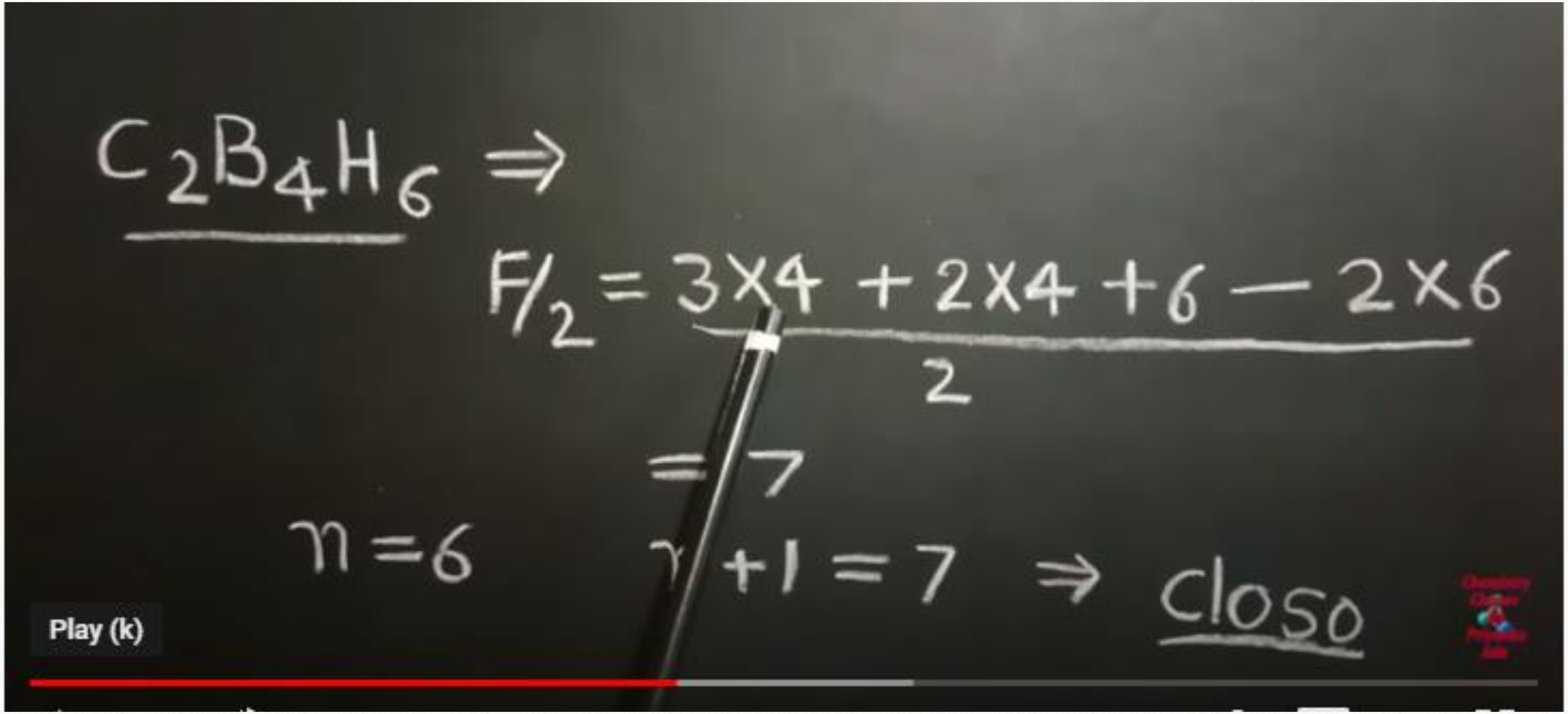
n = No of vertices (B + C)

* BH – group can be replaced by CH unit without the change in the value of F
* C , Si, Ge and Sn can be replaced by the BH unit
* N, P,As by BH_2 unit. * S,Se by BH_3 unit.



1) When F/2 = n+1 → Closo
with n vertex
(Triangulated, regular Polyhedron)
F/x → [BnHn]-2, [CBn-1Hn]-, [C2Bn-2Hn]
Ex B6H6-2 ⇒
F/2 = 3×6 + 1×6 + 2 − 2×6
2
Play (k)
Chemistry Classes By Priyanka Jain
3:59 / 12:54


Chemistry Classes
By
Priyanka Jain
Ex → B6H6−2 ⇒
= 3X6 + 1X6 + 2 − 2X6
2
= 7
n+1 = 7 ⇒ closo
Play (k)
4:36 / 12:54


C2B4H6 ⇒
F/2 = (3×4 + 2×4 + 6 − 2×6)/2
= 7
n = 6
+1 = 7 ⇒ closo
Play (k)

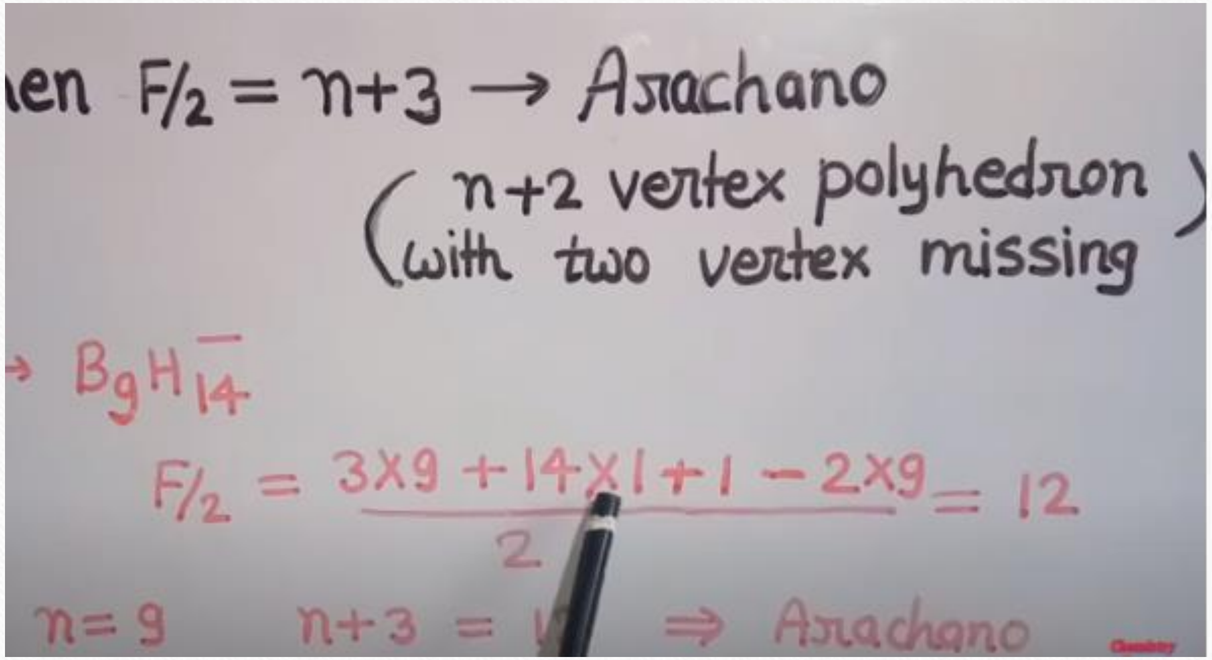
2) When $F/2 = n+2 \rightarrow$ <u>Nido</u>

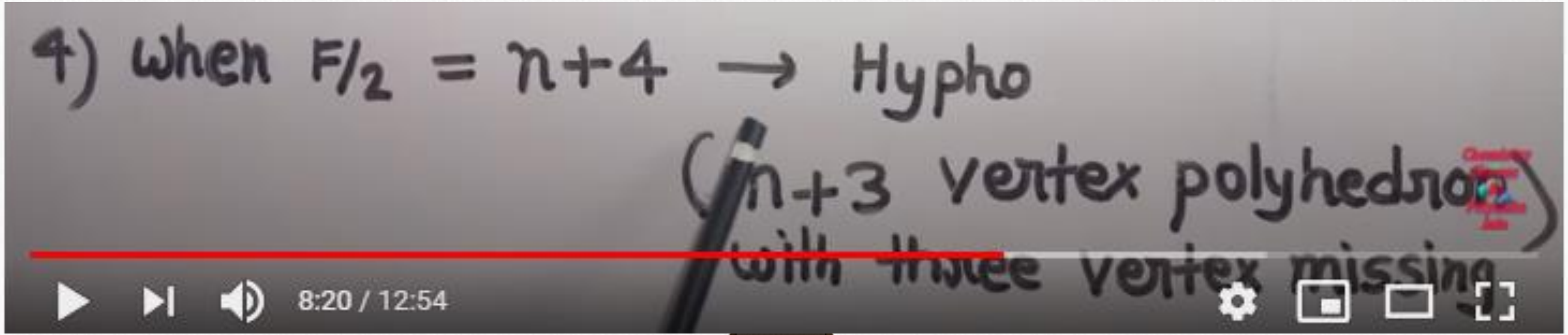
(with $n+1$ vertex polyhedral)
where 1 vertex is missing

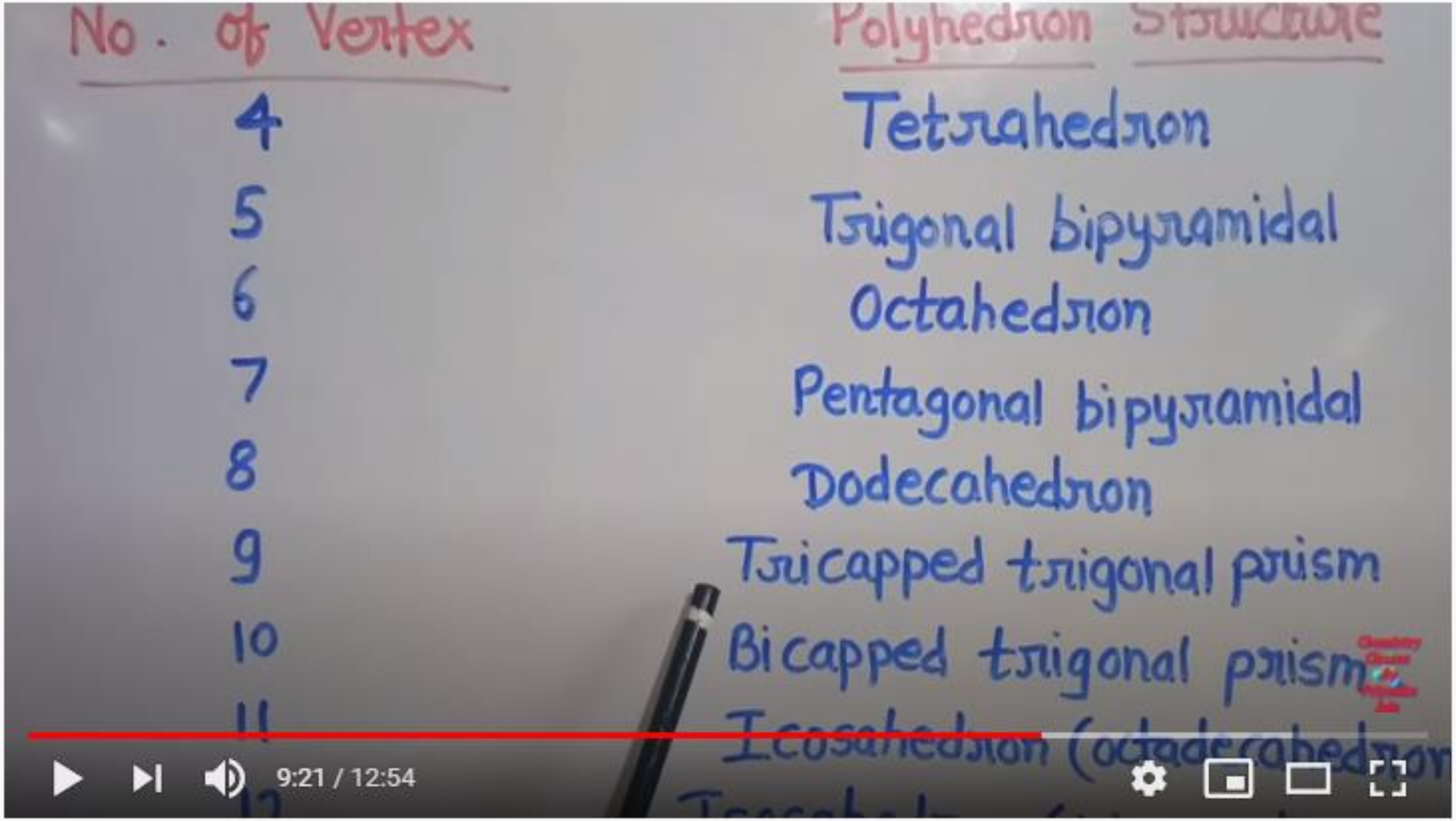
Ex $\rightarrow$ B_5H_9 $\Rightarrow$

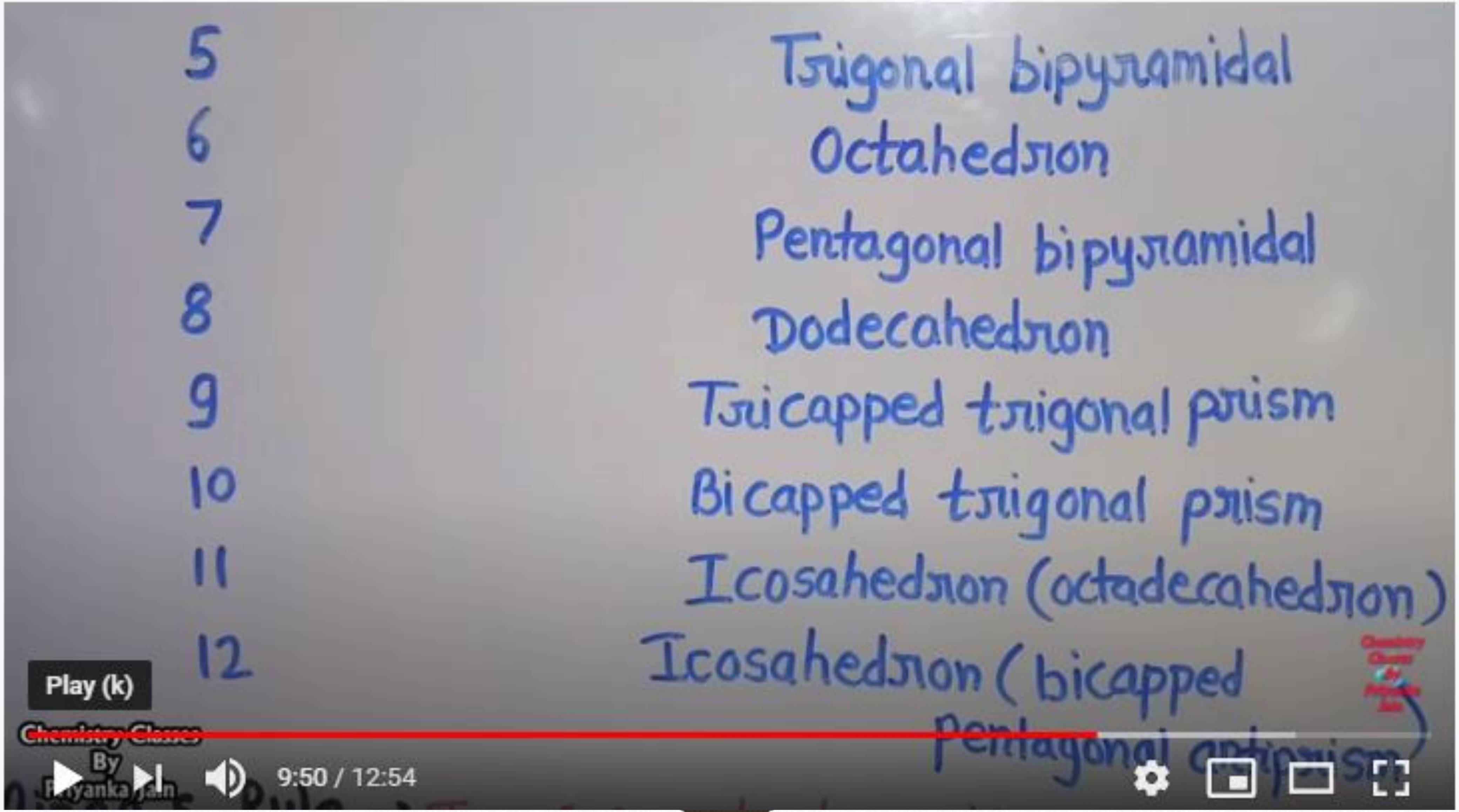
$$F/2 = \frac{3\times5 + 9\times1 - 2\times5}{2} = 7$$

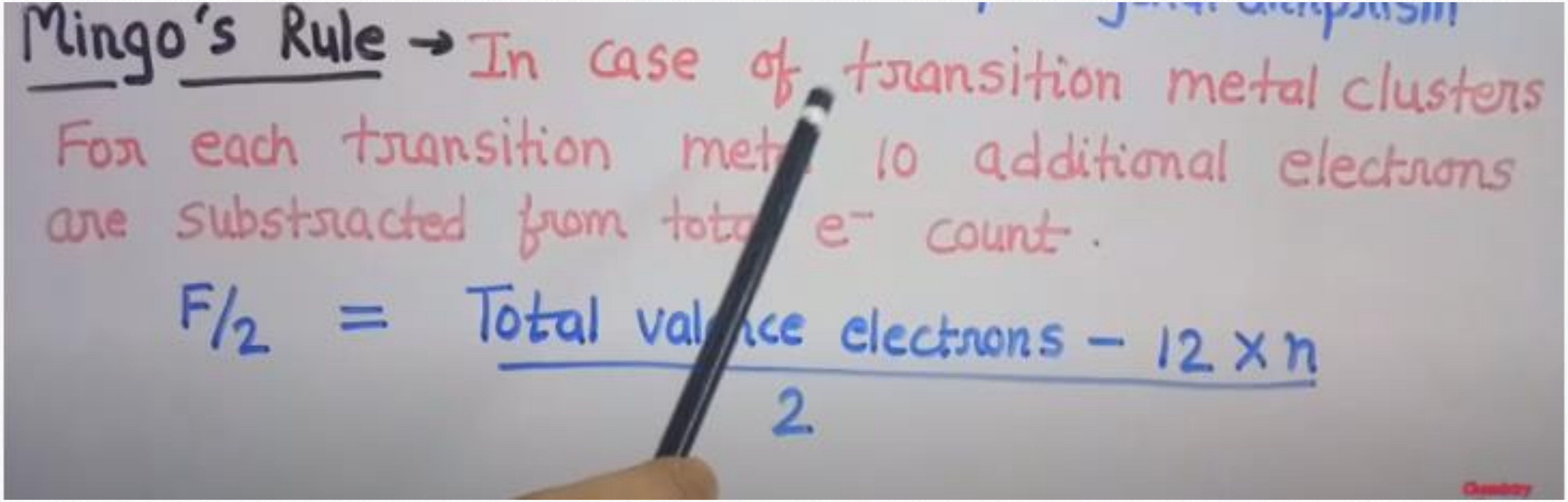
$n = 5 \quad n+2 = 7 \Rightarrow$ Nido


en F/2 = n+3 → Arachano
(n+2 vertex polyhedron
with two vertex missing)
→ B9H14
F/2 = 3x9 + 14x1 + 1 − 2x9 / 2 = 12
n = 9
n+3 =
⇒ Arachano


4) when F/2 = n+4 → Hypho
(n+3 vertex polyhedron
with three vertex missing
8:20 / 12:54


No. of Vertex
Polyhedron Structure
4
Tetrahedron
5
Trigonal bipyramidal
6
Octahedron
7
Pentagonal bipyramidal
8
Dodecahedron
9
Tricapped trigonal prism
10
Bicapped trigonal prism
11
9:21 / 12:54


5 Trigonal bipyramidal
6 Octahedron
7 Pentagonal bipyramidal
8 Dodecahedron
9 Tricapped trigonal prism
10 Bicapped trigonal prism
11 Icosahedron (octadecahedron)
12 Icosahedron (bicapped pentagonal antiprism)
Play (k)
Chemistry Classes By Priyanka Jain
9:50 / 12:54



Mingo's Rule → In case of transition metal clusters
For each transition met 10 additional electrons
are substracted from tot e⁻ count.
$F/2 = \frac{\text{Total val ce electrons} - 12 \times n}{2}$

Ex ⇒ $Rh_6(CO)_{16}$

$$F/2 = \frac{6 \times 9 + 16 \times 2 - 12 \times 6}{2}$$

$$= \frac{86 - 72}{2} = 7$$

$n =$ $n + 1 = 7$ Closo

$$\frac{S_4^{+2}}{} \Rightarrow \quad F = 4n + 2 \rightarrow \text{Closo}$$

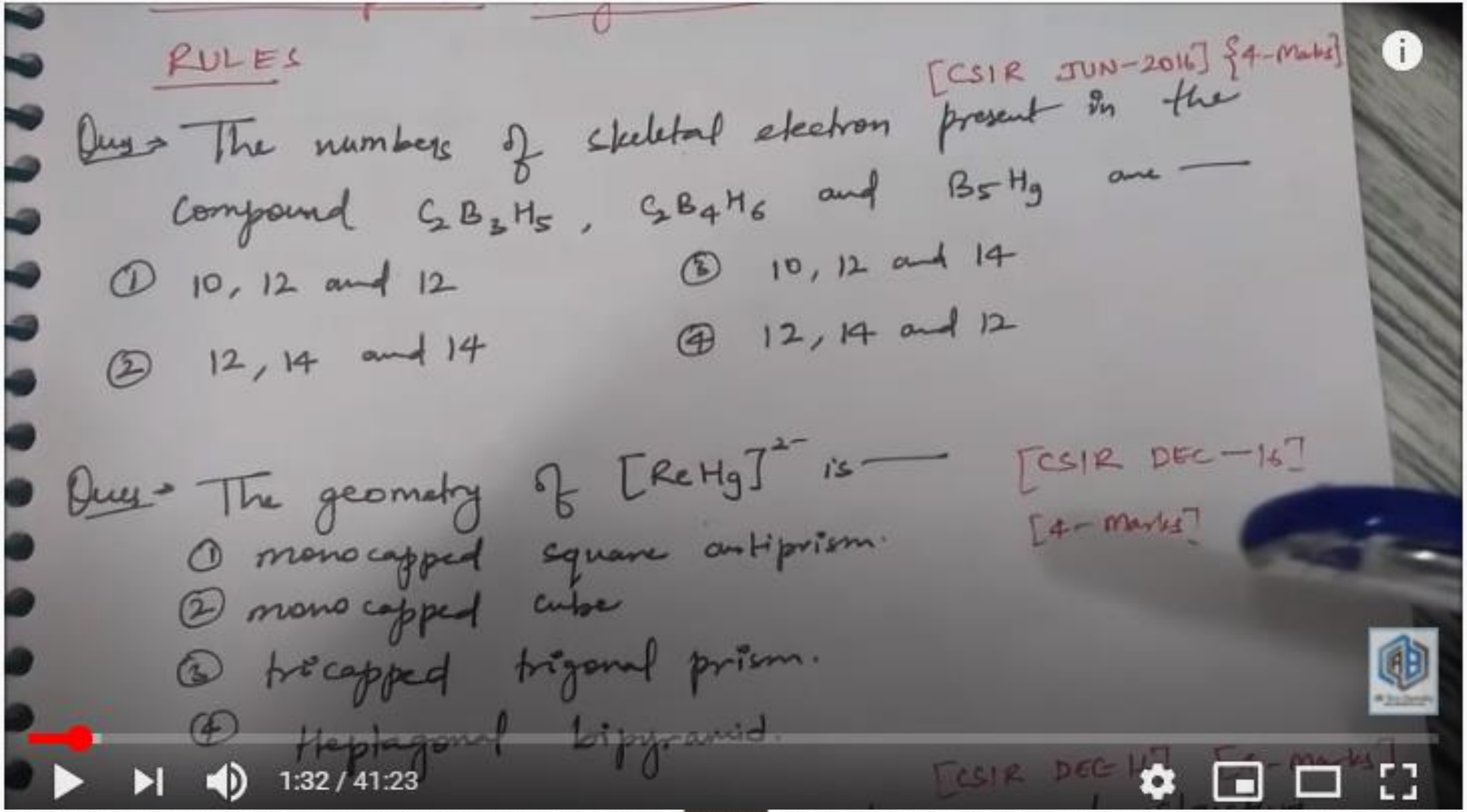
$$4n + 4 \rightarrow \text{Nido}$$

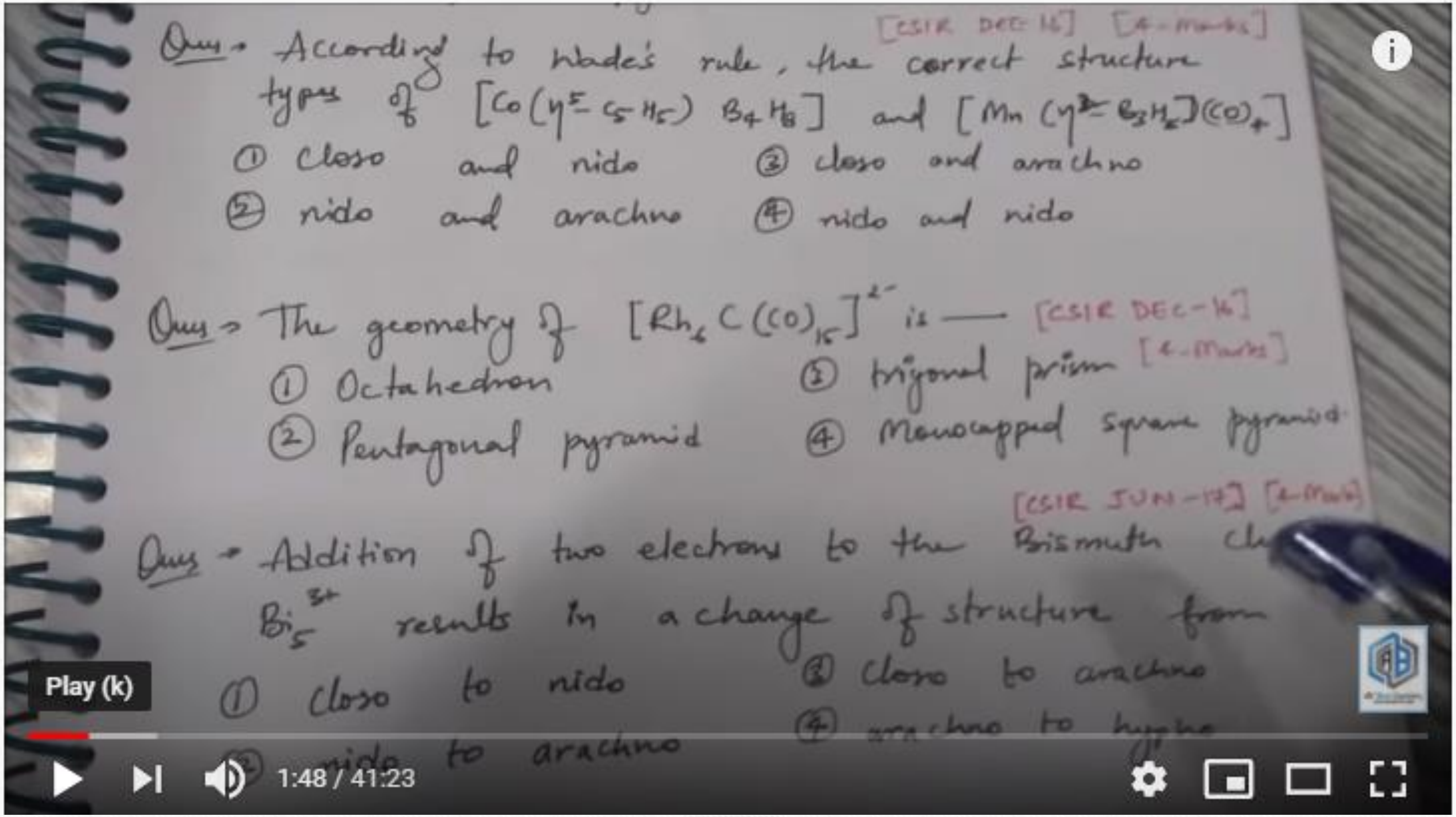
$$4n + 6 \rightarrow \text{Arachano}$$

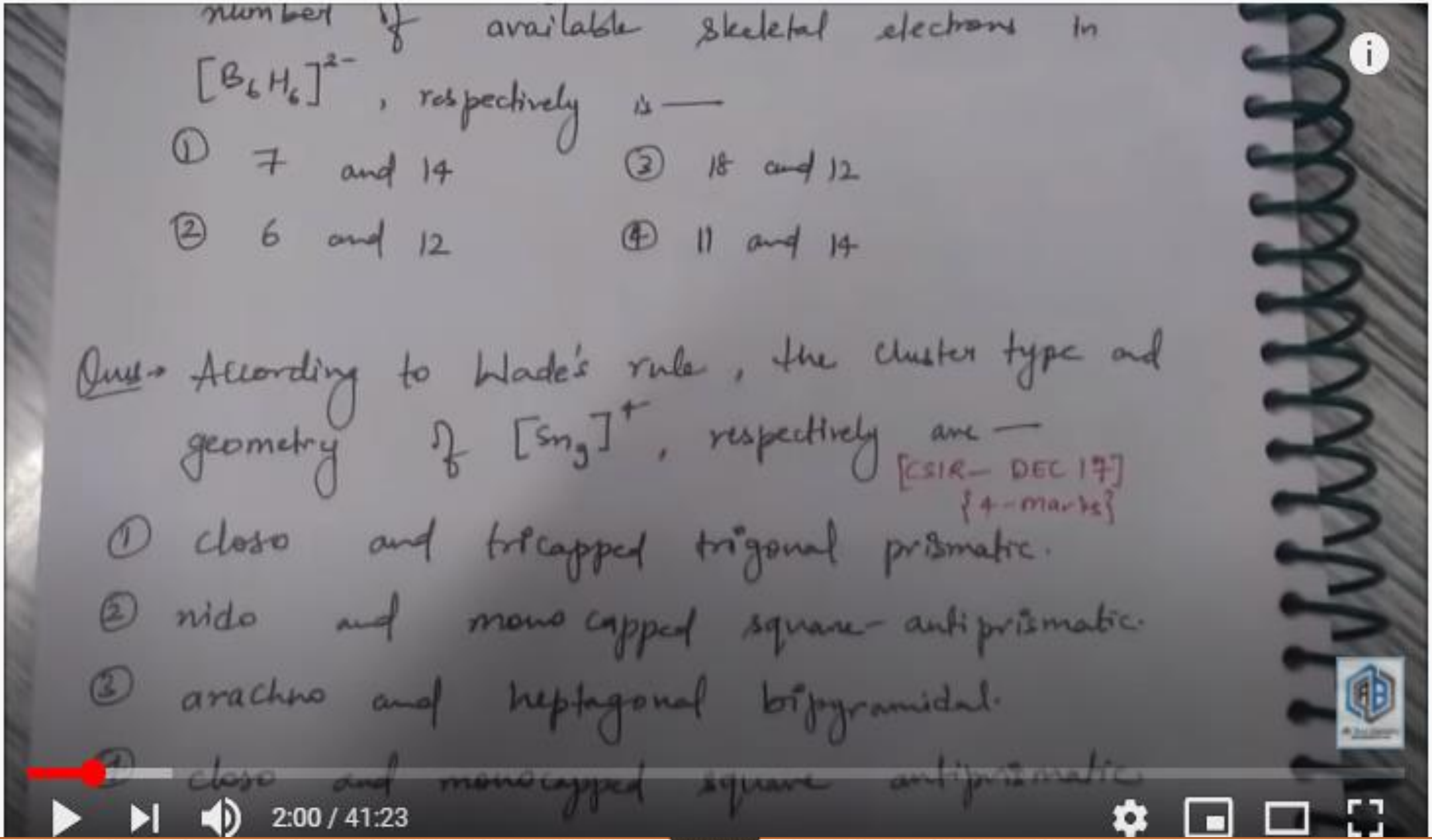
$$F = 4 \times 6 - 2 = 22$$

$$n = 4$$

$$4n + 6 = 22 \rightarrow \underline{\text{Arachano}}$$


RULES
[CSIR JUN-2016] {4-Marks}
Ques→ The numbers of skeletal electron present in the compound C2B3H5, C2B4H6 and B5H9 are ——
① 10, 12 and 12
③ 10, 12 and 14
② 12, 14 and 14
④ 12, 14 and 12
Ques→ The geometry of [ReH9]2− is ——
[CSIR DEC-16]
[4-Marks]
① monocapped square antiprism.
② mono capped cube
③ tricapped trigonal prism.
④ Heptagonal bipyramid.
1:32 / 41:23


Ques. According to Wade's rule, the correct structure types of [Co(η⁵-C₅H₅) B₄H₈] and [Mn (η³-B₃H₈)(CO)₄]
[CSIR DEC-16] [4-Marks]
① closo and nido
③ closo and arachno
② nido and arachno
④ nido and nido
Ques. The geometry of [Rh₆C(CO)₁₅]²⁻ is ——
[CSIR DEC-16] [4-Marks]
① Octahedron
③ trigonal prism
② Pentagonal pyramid
④ Monocapped square pyramid
[CSIR JUN-17] [4-Marks]
Ques. Addition of two electrons to the Bismuth cl
Bi₅³⁺ results in a change of structure from
① closo to nido
③ closo to arachno
② nido to arachno
④ arachno to hypho
Play (k)
1:48 / 41:23



number of available skeletal electrons in $[B_6H_6]^{2-}$, respectively is —

① 7 and 14
② 6 and 12
③ 18 and 12
④ 11 and 14

Ques→ According to Wade's rule, the cluster type and geometry of $[Sn_9]^{+}$, respectively are —

[CSIR– DEC 17]
{4-marks}

① closo and tricapped trigonal prismatic.
② nido and mono capped square-antiprismatic.
③ arachno and heptagonal bipyramidal.
④ closo and monocapped square antiprismatic