❖ Wade's Rules

Though the Lipscomb's topological model involving STYX numbers and rules was good in the rationalization of structures of some of the boranes and related species, it was not enough to higher boranes and carbonyl clusters. Therefore, a more sophisticated and comprehensive method was needed. In 1971, a British chemist, Kenneth Wade, published a revolutionary paper in the field of cluster chemistry. The main outlines of this communication were later to be called as Wade's rules, which provided a straightforward and elegant explanation of the geometries of ''electron-deficient'' cluster compounds in terms of the number of skeletal electron pairs (SEPs) available. The main focus of this paper was on boranes, carboranes and low-valent transition-metal clusters; whose structures could not be explained by the normal 2-center-2-electron bond. After Wade's initial report, another British chemist, Michael Mingos, extended the principles of counting skeletal electron pairs to electron-precise and electron-rich clusters and gave a more generalized way of calculating the skeletal electron contribution of a wide range of transition-metal. Thereafter, the rules became known as the Wade-Mingos rules or, more formally, the polyhedral skeletal electron pair theory (PSEPT).

The structure prediction is based on different sets of rules (4*n*, 5*n*, or 6*n*), which are developed on the basis of the number of electrons present per vertex. The 4*n* rules are pretty much accurate in predicting the structures of clusters with 4 electrons per vertex, as is the case for many carboranes or boranes. The clusters following 4*n* rule are generally classified as closo-, nido-, arachno- or hypho-, depending on whether they represent a complete (closo-) deltahedron, or a deltahedron that is missing one (nido-), two (arachno-) or three (hypho-) vertices. However, if the count of electrons is near to 5 electrons per vertex, the structure changes occur and are governed by the 5*n* rules (based on 3-connected polyhedrons). Moreover, if the electron count is increased further, the clusters with 5*n* electron counts become very unstable, and the 6*n* rules find their role. The cluster compounds following 6*n* rule have structures that are dependent on rings.

➢ *4n Rule*

The basis closo-polyhedra for the 4*n* rules are composed of triangular faces. The number of vertices in the cluster prediction and the corresponding basis polyhedron is given below.

Table 8. Base polyhedrons for structure prediction using 4*n* rule.

No. of Vertex	Polyhedron	No. of Vertex	Polyhedron
4	Tetrahedron	9	Tricapped trigonal prism
5	Trigonal bipyramid	10	Bicapped square antiprism
6	Octahedron	11	Octadecahedron
7	Pentagonal bipyramid	12	Icosahedron
8	D_{2d} (trigonal) dodecahedron		

Using the electron count, the predicted structure can be found. n is the number of vertices in the cluster. The $4n$ rules are enumerated in the following table.

Table 9. Electron count and predicted structure using $4n$ rule.

Electron count	Name	Predicted structure
$4n - 2$	Bicapped closo	$n - 2$ vertex closo polyhedron with 2 capped faces
$4n$	Capped closo	$n - 1$ vertex closo polyhedron with 1 face capped
$4n + 2$	Closo	Closo polyhedron with n vertices
$4n + 4$	Nido	$n + 1$ vertex closo polyhedron with 1 missing vertex
$4n + 6$	Arachno	$n + 2$ vertex closo polyhedron with 2 missing vertex
$4n + 8$	Hypho	$n + 3$ vertex closo polyhedron with 3 missing vertex
$4n + 10$	Klado	$n + 4$ vertex closo polyhedron with 4 missing vertex

The valence electrons are enumerated when the counting of electrons for each cluster is carried out. For each transition metal atom or ion present, ten electrons are subtracted from the total number of electrons. For example, in $Rh_6(CO)_{16}$ the total number of electrons would be $6 \times 9 + 16 \times 2 - 6 \times 10 = 86 - 6 \times 10 = 26$. Therefore, the cluster is a closo polyhedron because $n = 6$, with $4n + 2 = 26$. When structure prediction is carried out, other postulates may be given as:

i) For clusters that are comprised mainly of transition metals, any main group atoms are generally counted as ligands or interstitial atoms, and not vertices.

ii) Larger atoms or more electropositive groups have the tendency to occupy vertices of higher connectivity; while the smaller or more electronegative atoms tend to fill vertices of low connectivity.

iii) In some special boron hydride clusters, every boron connected to 3 or more vertices has one terminal H, while a boron connected to two other vertices has two terminal H. Any extra hydrogens left are placed in open-face positions to even out the coordination number of different vertices.

iv) In some special cases of transition metal clusters, ligands are added to the metal centers to impart the metals a reasonable coordination numbers, and if any H atoms are present, they should be placed in bridging sites to even out the coordination numbers of different vertices.

Generally speaking, closo clusters with n vertices are n-vertex polyhedral structures. To find the nido-cluster structure, a closo cluster with $n + 1$ vertices is exploited as a starting point; if the cluster is consisted of small atoms, a vertex with high connectivity is removed; while if the cluster is consisted of large atoms, a vertex with low-connectivity is removed. To find the structure of arachno clusters, a closo polyhedron with n+2 vertices is exploited as the starting point, and a nido complex with n+1 vertex is created by the rule

discussed above. However, if the cluster is of small atoms, a second vertex which adjacent to the first is removed; and if the cluster is of large atoms mainly, the second vertex removed is not adjacent to the first one.

Examples: i) P_4: Electron count = 4 × number of valence electron of P = 4 × 5 = 20 electrons. Since n = 4, $4n$ + 4 = 20, so the cluster is a nido borane. Starting from base polyhedron of n + 1 vertex, one vertex has to be removed. Here, starting from trigonal bipyramid and removing one axial vertex gives the tetrahedral cluster.

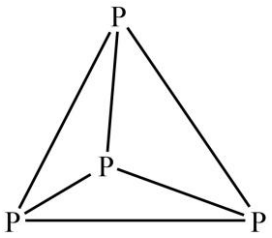


Figure 10. Structure of P_4.

ii) S_4^{2+}: Electron count = 4 × number of valence electron of S = 4 × 6 −2 (for charge) = 22 electrons. Since n = 4, $4n$ + 6 = 22, so the cluster is an arachno borane. Starting from base polyhedron of n + 2 vertex, two vertexes have to be removed. In this case, it will start from octahedron and then the removal of two non-adjacent vertexes will give square cluster.

Figure 11. Structure of S_4^{2+}.

iii) $B_5H_5^{4-}$: Electron count = 5 × 3 + 1 × 5 + 4 = 24 electrons. Since n = 5, $4n$ + 4 = 24, so the cluster is a nido borane. In this case, will start from octahedron and then the removal of one vertexes will give square pyramidal. The hydrogens have been omitted for clarity.

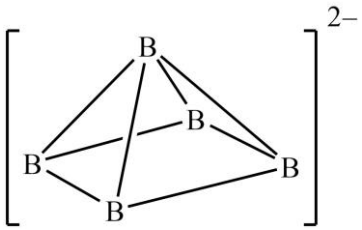


Figure 12. Structure of $B_5H_5^{4-}$.

iv) $Os_6(CO)_{18}$: Electron count: 6 × Os + 18 × CO – 60 (for 6 osmium atoms) = 6 × 8 + 18 × 2 – 60 = 24. Since $n = 6$, $4n = 24$, so the cluster is capped closo. Starting from a trigonal bipyramid, a face is capped. The carbonyls have been omitted for clarity.

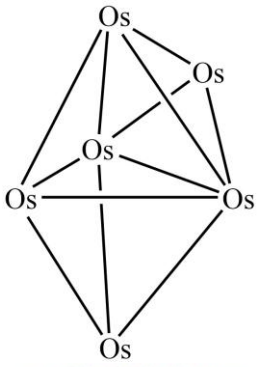


Figure 13. Structure of $Os_6(CO)_{18}$.

v) $C_2B_5H_7$: Electron count = 2 × C + 5 × B + 7 × H = 2 × 4 + 3 × 5 + 7 × 1 = 30. Since n in this case is 7, $4n + 2 = 30$, the cluster is closo. The hydrogens have been omitted for clarity.

Figure 14. Structure of $C_2B_5H_7$.

The bookkeeping for deltahedral clusters is sometimes carried out by counting skeletal electrons pairs instead of the total number of electrons. The CH and BH units are considered as 3 and 2 electron donor, respectively. Additional hydrogen contributes 1 electron and charge is considered as it is. m is the sum of the number of boron and carbon atoms.

No. of *e* pair	$m - 1$	m	$m + 1$	$m + 2$	$m + 3$	$m + 4$	$m + 5$
Structure	Bicapped closo	Capped closo	Closo	Nido	Arachno	Hypho	Klado

For example, in $C_2B_7H_{13}$, m is 9, while electron pairs are 2 × CH + 7 × BH + 4 × H = 6 + 14 + 4 = 24 or 12 pairs. The number of framework electron pairs are 9 + 3 = 12; hence the structure is arachno.

➢ ***5n Rule***

If electrons per vertex are approaches 5, the 5*n* rule is used based on a different series of polyhedra known as the 3-connected polyhedra, in which each vertex is connected to 3 other vertices.

Table 10. Base polyhedrons for structure prediction using 5*n* rule.

No. of Vertex	Polyhedron	No. of Vertex	Polyhedron
4	Tetrahedron	14	Dual of triaugmented triangular
6	Trigonal prism	16	Square truncated trapezohedron
8	Cube	18	Dual of edge-contracted icosahedron
10	Pentagonal prism	20	Dodecahedron
12	D_{2d} pseudo-octahedron		

The 5*n* rules are as follows:

Table 11. Electron count and predicted structure using 5*n* rule.

Electron count	Predicted structure
5*n*	*n*-vertex 3-connected polyhedron
5*n* + 1	*n* – 1 vertex 3-connected polyhedron with one vertex inserted into an edge
5*n* + 2	*n* – 2 vertex 3-connected polyhedron with two vertexes inserted into an edge
5*n* + *k*	*n* – *k* vertex 3-connected polyhedron with *k* vertex inserted into an edge

Examples: i) P_4S_3: Electron count = 4 × number of valence electron of P + 3 × number of valence electrons of S = 4 × 5 + 3 × 6 = 38 electrons. Since *n* = 7, 5*n* + 3 = 38. Three vertices are inserted into edges.

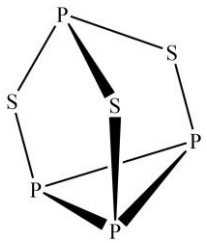


Figure 15. Structure of P_4S_3.

ii) P_4O_6: Electron count = 4 × number of valence electron of P + 6 × number of valence electrons of O = 4 × 5 + 6 × 6 = 56 electrons. Since n = 10, $5n + 6 = 56$. Six vertices are inserted into edges.

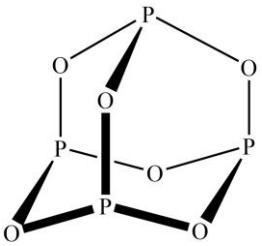


Figure 16. Structure of P_4O_6.

- ***6n Rule***

If the electron count per vertex is about 6, a $6n$ rule is used for structure prediction. This is because structures based on $4n$ or $5n$ rules would become unstable if the number of electron approaches 6, and clusters tend to give structures governed by the $6n$ rules. The rules for the 6n structures are as follows:

Table 12. Electron count and predicted structure using $6n$ rule.

Electron count	Predicted structure
$6n - k$	n-membered ring with $k/2$ transannular bonds
$6n - 4$	n-membered ring with 2 transannular bonds
$6n - 2$	n-membered ring with 1 transannular bond
$6n$	n-membered ring
$6n + 2$	n-membered chain (n-membered ring with 1 broken bond)

Examples: i) S_8: Electron count = 8 × number of valence electron of S = 48 electrons. Since n = 8, $6n$ = 48. Therefore, the cluster is an 8-membered ring.

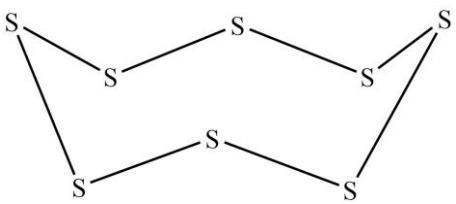


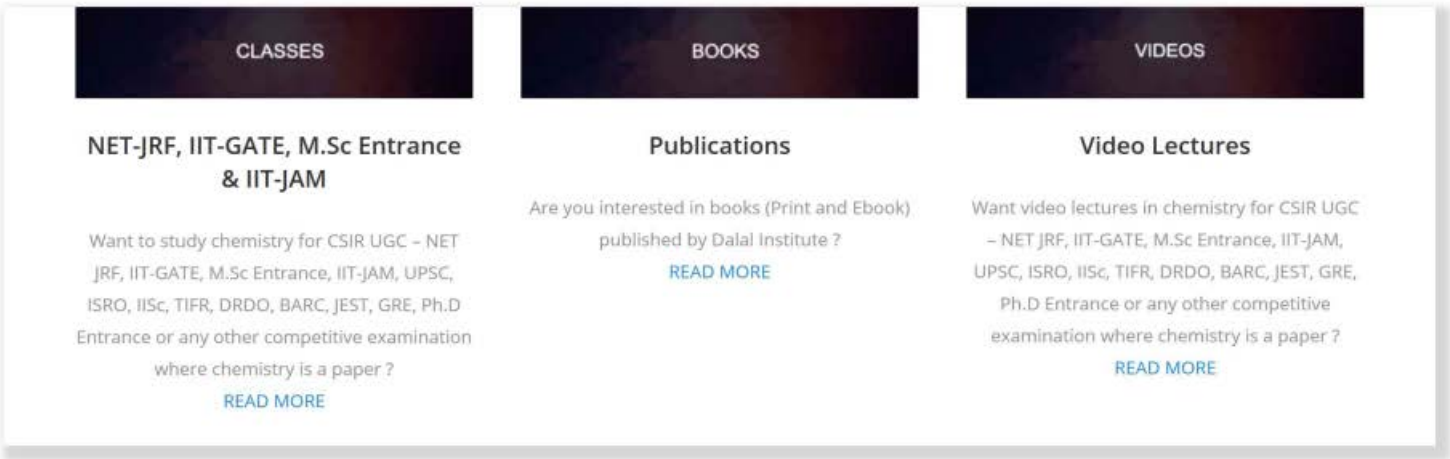
Figure 17. Structure of S_8.

ii) C_6H_{14}: Electron count = 6 × number of valence electron of C + 14 × number of valence electrons of H = 6 × 4 + 14 × 1 = 38 electrons. Since $n = 6$, $6n + 2 = 38$. Therefore, the cluster is a 6-membered chain.

Figure 18. Structure of C_6H_{14}.

It is also worth mentioning that Wade's rules not only rationalized the structures of a vast number of cluster compounds but they have also stimulated further research in cluster chemistry.

Home



Home: https://www.dalalinstitute.com/
Classes: https://www.dalalinstitute.com/classes/
Books: https://www.dalalinstitute.com/books/
Videos: https://www.dalalinstitute.com/videos/
Location: https://www.dalalinstitute.com/location/
Contact Us: https://www.dalalinstitute.com/contact-us/
About Us: https://www.dalalinstitute.com/about-us/

Postgraduate Level Classes (NET-JRF & IIT-GATE)
Admission
Regular Program Distance Learning
Test Series Result

Undergraduate Level Classes (M.Sc Entrance & IIT-JAM)
Admission
Regular Program Distance Learning
Test Series Result

A Textbook of Inorganic Chemistry – Volume 1

"A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal" is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.
READ MORE

International Edition

A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

MANDEEP DALAL

First Edition

DALAL INSTITUTE

Table of Contents

Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-0-0

MRP: Rs 800.00

DALAL INSTITUTE

Main Market, Sector 14, Rohtak, Haryana 124001, India
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com