

# AdiChemistry

## SELECTED & IMPORTANT TOPICS

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2019 Edition

(No of pages: 926)

FOR CSIR UGC NET - GATE - SET EXAMS

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### SALIENT FEATURES

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through  
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## SELECTED & IMPORTANT TOPICS

### WADE-MINGOS RULES (polyhedral skeletal electron pair theory) STUDY MATERIAL

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### WADE-MINGOS RULES

Wade-Mingo's rules can be applied to clusters like boranes and carboranes that have same deltahedral geometry. The polyhedra with triangular faces are usually referred to as deltahedra.

The type and structure of boranes and carboranes can be derived as follows:

#### Step-1:

First, the number of skeletal electrons are calculated as sum of the following contributions.

- \* Each B-H contributes 2.
- \* Each C-H contributes 3.
- \* Each additional hydrogen contributes 1.
- \* Finally the anionic charge on the cluster is to be added to above contributions.

i.e., Skeletal Electron Count (SE) =  $2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster}$

#### Step-2:

Now calculate the number of pairs of electrons (MO's).

$$\text{No. of Skeletal Electron Pairs (SEP)} = \frac{\text{Skeletal Electron count (SE)}}{2}$$

#### Step-3:

Let the number of vertices (no. of B & C atoms) is given by 'n'. Then by comparing the number of electron pairs with number of vertices (n), the cluster's structure can be derived as follows:

No. of Skeletal Electron Pairs(SEP)	Type of Borane
n+1	Closo
n+2	Nido
n+3	Arachno
n+4	Hypho
n+5	Clado

Note: 'n' is the number of vertices.

### ILLUSTRATIONS

#### 1) $B_7H_7^{2-}$ , Heptahydroheptaborate(2-)

$$\text{step-1: skeletal electron count} = 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ = 2(7) + 0 + 0 + 2 = 16$$

$$\text{step-2: no. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{16}{2} = 8$$

step-3: The no. of vertices =  $n = 7$   
no. of electron pairs = 8, which corresponds to  $n+1$ .  
Hence it is a closo borane (no vertex is missing).

\* As no vertex is missing, the cage structure should contain  $n=7$  vertices and is pentagonal bipyramidal

#### 2) $B_6H_{10}$ - Hexaborane(10)

$$\text{step-1: skeletal electron count} = 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ = 2(6) + 0 + 4 + 0 = 16$$

$$\text{step-2: no. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{16}{2} = 8$$

step-3: The no. of vertices =  $n = 6$   
no. of electron pairs = 8, which corresponds to  $n+2$ .  
Hence it is a nido borane (one vertex is missing)

\* As only one vertex is missing, the parent cage must contain  $n+1=7$  vertices. Hence the structure of  $B_6H_{10}$  must be pentagonal bipyramidal with one vertex missing (you can call it as pentagonal pyramid with 6 vertices)

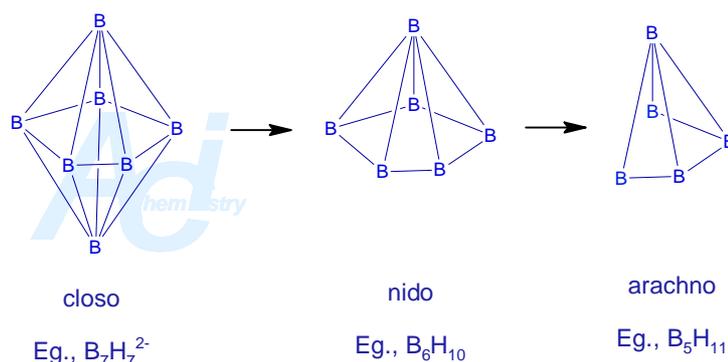
#### 3) $B_5H_{11}$ - Pentaborane(11)

$$\text{step-1: skeletal electron count} = 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ = 2(5) + 0 + 6 + 0 = 16$$

$$\text{step-2: no. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{16}{2} = 8$$

step-3: The no. of vertices =  $n = 5$   
no. of electron pairs = 8, which corresponds to  $n+3$ .  
Hence it is an arachno borane (two vertices are missing).

\* As two vertices are missing the parent cage must contain  $n+2 = 7$  vertices. Hence the cage structure of  $B_5H_{11}$  is pentagonal bipyramidal with two vertices missing.



Only the positions of boron atoms are shown. Lines may or may not represent the actual bonds between them.

#### 4) $C_2B_7H_{13}$

step-1: skeletal electron count =  $2(B-H) + 3(C-H) + 1(\text{addtl.H}) + \text{anionic charge on cluster}$   
 $= 2(7) + 3(2) + 4 + 0 = 24$

step-2: no. of electron pairs =  $\frac{\text{skeletal electron count}}{2} = \frac{24}{2} = 12$

step-3: The no. of vertices =  $n = 9$   
 no. of electron pairs = 12, which corresponds to  $n+3$ .  
 Hence it is an arachno carborane (two vertices are missing).

\* The parent cage must contain  $n+2 = 11$  vertices, which corresponds to edge-contracted icosahedron (octadecahedron). Hence the cage structure of  $C_2B_7H_{13}$  is edge-contracted icosahedron (octadecahedron) with two vertices missing.

### THEORY BEHIND WADE-MINGO'S RULES

\* The number of valence electrons in boron is 3. Among them, one electron is contributed for B-H bond at the vertex. The remaining 2 electrons are involved in skeletal bonds formation and are termed as skeletal electrons (SE's). That is why contribution of each B-H to skeletal electrons is 2.

Likewise, carbon contributes 3 electrons to the skeleton.

\* A closo-deltahedral cluster cage with 'n' vertices requires (n+1) skeletal electron pairs (SEP's) which occupy (n+1) cluster bonding MOs ; It also implies, the skeletal electrons (SE's) must be equal to  $2n+2$ . (i.e. n vertices require  $2n+2$  electrons in closo cluster)

\* Likewise, a nido-deltahedral cluster cage with 'n' vertices requires (n+2) pairs of electrons and so on.

Note: Here the value of 'n' represents the actual number of vertices in the cluster (or the number of boron as well as carbon atoms). According to some textbooks, 'n' represents the number of vertices in the parent closo cluster.

**APPLICATION TO CLUSTERS OF MAIN GROUP**

\* Wade's rules may be applied to naked clusters formed by p-block elements by assuming each atom contains a localized non-bonding lone pair.

**Examples:**

1) In  $[\text{Pb}_5]^{2-}$ , the no. of valence electrons + charge =  $5(4) + 2 = 22$ .

Among them,  $5 \times 2 = 10$  electrons are in lone pairs.

Hence the number of SEs =  $22 - 10 = 12$

Now the number of SEPs =  $12/2 = 6$

As no. of SEPs corresponds to  $n+1 = 5+1 = 6$ ,  $[\text{Pb}_5]^{2-}$  must have 'closo' structure. (Here the no. of Pb atoms = 5)

2) In  $\text{P}_4$  molecule, the no. of valence electrons + negative charge =  $4(5) + 0 = 20$

Among them, 8 electrons are in lone pairs.

Hence the no. of SEs =  $20 - 8 = 12$

Now the no. of SEPs =  $12/2 = 6$

As the no. of SEPs corresponds to  $n+2 = 4 + 2 = 6$ ,  $\text{P}_4$  must have 'nido' structure.

V. Aditya Vardhan

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**CLUSTER VALENCE ELECTRON THEORY**

This is a second method for determining the geometry of a cluster. It is more comprehensive and works for all boranes, as well as related carboranes.

To use this method, the total number of valence electrons used in cluster bonding must be determined.

- \* Boron contributes 3 valence electrons.
- \* Carbon contributes 4 valence electrons.
- \* Hydrogen contributes 1 valence electron.
- \* The total negative charge must be added to above contributions.

The structure is determined according to the following equations:

closo -  $4n + 2$  valence electrons

nido -  $4n + 4$  valence electrons

arachno -  $4n + 6$  valence electrons

Hypho -  $4n + 8$  valence electrons

where  $n$  = number of boron atoms in the cluster

**Example:****1)  $B_7H_7^{2-}$ , Heptahydroheptaborate(2-)**

$$4n = 4 \times 7 = 28$$

$$\text{Total no. of valence electrons} = 7(3) + 7(1) + 2 = 30$$

Since there are  $4n+2$  electrons ( $30 = 28 + 2$ ), it must be a closo borane.

**APPLICATION TO CLUSTERS OF TRANSITION ELEMENTS**

This approach is also be used for transition metal clusters. First, the total number of valence electrons used in the skeleton of the cluster formation is calculated as follows:

- \* Each monodentate ligand contributes 2 electrons.
- \* Metal contributes its  $(n-1)d$  and  $ns$  electrons.
- \* Finally any negative charge on the cluster must be added.

The structure is determined according to the following equations:

closo -  $14n + 2$  valence electrons

nido -  $14n + 4$  valence electrons

arachno -  $14n + 6$  valence electrons

Hypho -  $14n + 8$  valence electrons

where  $n$  = number of vertices or metal atoms in the cluster.

**1)  $Rh_6(CO)_{16}$  :**

$$14n = 14 \times 6 = 84$$

Rh belongs to group 9. Hence the # valence electrons in it is 9 (both d and s electrons)

$$\text{Total valence electron count} = 6(9) + 16(2) = 86.$$

There are  $4n+2 = 84 + 2$  valence electrons and hence a 'closo' cluster.

**SOLVED QUESTIONS**

1) Which one of the following boranes is classified as a nido-borane?

- 1)  $B_2H_6$       2)  $B_2H_7^-$       3)  $B_4H_{10}$       4)  $B_{12}H_{12}^{2-}$

**Answer & explanation:**

$B_2H_6$  is a nido-borane as it has  $B_nH_{n+4}$  formula.

By using Wade's rules:

$$\begin{aligned} \text{skeletal electron count} &= 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ &= 2(2) + 3(0) + 1(4) + 0 = 8 \end{aligned}$$

$$\text{no. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{8}{2} = 4$$

The no. of vertices =  $n = 2$

no. of electron pairs = 4, which corresponds to  $n+2$ .

Hence it is a nido borane (one vertex is missing)

2) Which of the following is an arachno borane?

- 1)  $[B_6H_6]^{2-}$       2)  $B_5H_9$       3)  $B_2H_6$       4)  $B_6H_{12}$

**Answer & explanation:**

$[B_6H_{12}]$  is an arachno-borane as it has  $B_nH_{n+6}$  formula. (Use Wade's rules to justify this)

3) The structure and the number of isomers of  $B_{10}C_2H_{12}$  respectively are: (GATE 2003)

- a) nido & 2      b) closo & 3      c) nido & 1      d) closo & 2

**Answer & explanation:**

Application of Wade's rules for  $B_{10}C_2H_{12}$

$$\begin{aligned} \text{skeletal electron count} &= 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ &= 2(10) + 3(2) + 1(0) + 0 = 26 \end{aligned}$$

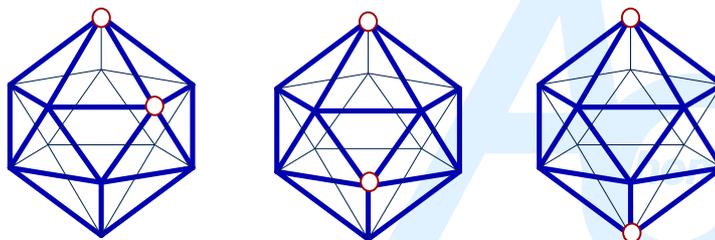
$$\text{no. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{26}{2} = 13$$

The no. of vertices =  $n = 12$

no. of electron pairs = 13, which corresponds to  $n+1$ .

Hence it is a closo borane (NO vertex is missing)

It has Icosahedral structure. 3 isomers are possible as shown below.



Three isomers are possible. The relative positions of Carbon atoms are shown by circles.

4)  $B_{10}C_2H_{12}$  is isoelectronic with:

(GATE 1996)

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- a)  $B_{12}H_{12}^{2-}$       b)  $B_{12}H_{12}$       c)  $B_{12}H_{12}^{+}$       d)  $B_{12}H_{12}^{2+}$

Ans: a)

**Explanation:** Each carbon contributes one excess of electron than boron.

- 5) The number of 'framework electron pairs' present borane cluster  $[B_{12}H_{12}]^{2-}$  is:  
(GATE 2010)

- a) 10      b) 11      c) 12      d) 13

**Answer & Explanation:** E.g.  $B_{12}H_{12}^{2-}$ , Dodecahydrododecaborate(2-)

$$\text{step-1: skeletal electron count} = 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ = 2(12) + 0 + 0 + 2 = 26$$

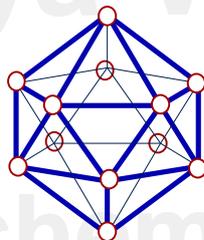
$$\text{step-2: no. of electron pairs} = \frac{\text{skeletal electron count}}{2} = \frac{26}{2} = 13$$

step-3: The no. of vertices = n = 12

no. of electron pairs = 13, which corresponds to n+1.

Hence it is a closo borane (no vertex is missing).

\* As no vertex is missing, the cage structure should contain n=12 vertices and is icosahedral.



- 6) Which of the following is an arachno borane? (GATE 2000)

- a)  $[B_6H_6]^{2-}$       b)  $[B_5H_9]$       c)  $[B_2H_6]$       d)  $[B_6H_{12}]$

**Explanation:**

By using Wade's rules:

**For  $[B_6H_6]^{2-}$**

$$\text{skeletal electron count} = 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ = 2(6) + 3(0) + 1(0) + 1(2) = 14$$

$$\text{no. of skeletal electron pairs} = 14/2 = 7$$

The no. of vertices = n = 7

no. of electron pairs = 7, which corresponds to n+1.

Hence it is a closo borane (no vertex is missing)

**For  $[B_5H_9]$**

$$\text{skeletal electron count} = 2(\text{B-H}) + 3(\text{C-H}) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ = 2(5) + 3(0) + 1(4) + 1(0) = 14$$

$$\text{no. of skeletal electron pairs} = 14/2 = 7$$

The no. of vertices = n = 5

no. of electron pairs = 7, which corresponds to n+2.

Hence it is a nido borane (one vertex is missing)

For  $[B_2H_6]$

$$\begin{aligned} \text{skeletal electron count} &= 2(B-H) + 3(C-H) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ &= 2(2) + 3(0) + 1(4) + 1(0) = 8 \end{aligned}$$

$$\text{no. of skeletal electron pairs} = 8/2 = 4$$

The no. of vertices =  $n = 2$

no. of electron pairs = 4, which corresponds to  $n+2$ .

Hence it is a nido borane (one vertex is missing)

For  $[B_6H_{12}]$

$$\begin{aligned} \text{skeletal electron count} &= 2(B-H) + 3(C-H) + 1(\text{addtl.H}) + \text{anionic charge on cluster} \\ &= 2(6) + 3(0) + 1(6) + 1(0) = 18 \end{aligned}$$

$$\text{no. of skeletal electron pairs} = 18/2 = 9$$

The no. of vertices =  $n = 6$

no. of electron pairs = 9, which corresponds to  $n+3$ .

Hence it is an arachno borane (two vertices are missing)

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## PRACTICE MULTIPLE CHOICE QUESTIONS

Keys/Solutions along with extra problems (updates) are available at <http://www.adichemistry.com/csir-net/chemistry/key.html>

- 1) According to Wade's rules, the structures of  $B_{10}C_2H_{12}$  and  $[B_9C_2H_{11}]^{2-}$  are respectively,  
 a) closo & arachno  
 b) closo & nido  
 c) nido & closo  
 d) nido & arachno  
 (GATE 2009)
- 2) Using Wade's rules predict the structure type of  $[C_2B_5H_7]$ .  
 1) nido  
 2) closo  
 3) arachno  
 4) hypho  
 (CSIR NET DEC 2015)
- 3)  $B_{10}C_2H_{12}$  is isoelectronic with  
 a)  $B_{12}H_{12}^{2-}$   
 b)  $B_{12}H_{12}$   
 c)  $B_{12}H_{12}^+$   
 d)  $B_{12}H_{12}^{2+}$
- 4) White phosphorus,  $P_4$ , belongs to the  
 a) closo system  
 b) nido system  
 c) arachno system  
 d) hypho system  
 (GATE 2008)
- 5) The correct classification of  $[B_5H_5]^{2-}$ ,  $B_5H_9$  and  $B_5H_{11}$  respectively is:  
 1) closo, arachno, nido  
 2) closo, closo, nido  
 3) arachno, closo, nido  
 4) closo, nido, arachno
- 6)  $Co_4(CO)_{12}$  adopts:  
 1) closo-structure  
 2) Nido-structure  
 3) Arachno-structure  
 4) Hypho-structure  
 (CSIR NET DEC 2014)
- 7) Boranes with formula  $B_nH_n^+$  have  
 a)  $n$  bonding orbitals and  $n$  antibonding orbitals  
 b) total  $2n+4$  electrons in bonding orbitals  
 c)  $n+1$  framework bonding orbitals  
 d) framework with  $n$  corners of  $(n+2)$  cornered polyhedron.
- 8) The numbers of skeletal electrons present in the compounds  $C_2B_3H_5$ ,  $C_2B_4H_6$  and  $B_5H_9$ , respectively, are:  
 1) 10, 12 and 12  
 2) 12, 14 and 14  
 3) 10, 12 and 14  
 4) 12, 14 and 12  
 (CSIR NET JUNE 2016)

"The law is reason free from passion"

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- 9) According to Wade's theory the anion  $[B_{12}H_{12}]^{2-}$  adopts (CSIR NET JUNE 2015)  
 1) closo-structure 2) arachno-structure 3) hypo-structure 4) nido-structure
- 10) Total number of vertices in metal clusters  $[Ru_6(C)(CO)_{17}]$ ,  $[Os_5(C)(CO)_{15}]$  and  $[Ru_5(C)(CO)_{16}]$  are 6, 5 and 5, respectively. The predicted structures of these complexes, respectively, are: (CSIR NET JUNE 2015)  
 1) Closo, nido and nido 2) Closo, nido and arachno  
 3) Arachno, closo and nido 4) Arachno, nido and closo
- 11) According to Wade's rules, the correct structural types of  $[Co(\eta^5-C_5H_5)B_4H_8]$  and  $[Mn(\eta^2-B_3H_8)(CO)_4]$  are: (CSIR NET DEC 2016)  
 1) closo and nido 2) nido and arachno  
 3) closo and arachno 4) nido and nido
- 12) According to Wade's rules, the cluster type and geometry of  $[Sn_9]^+$ , respectively, are (CSIR NET DEC 2017)  
 1) closo and tricapped trigonal prismatic  
 2) nido and monocapped square-antiprismatic  
 3) arachno and heptagonal bipyramidal  
 4) closo and monocapped square antiprismatic
- 13) According to Wade's rule, the structures of  $B_{10}C_2H_{12}$  and  $[B_9C_2H_{11}]^{2-}$ , respectively, are: (KERALA SET 2013) (GATE 2004)  
 A) closo and arachno B) nido and closo  
 C) closo and nido D) nido and arachno
- 14) Based on Wade's rule, the predicted structure of the metal cluster  $[Fe_4C(CO)_{12}]^{2-}$  is: (KARNATAKA SLET 2014)  
 (A) Nido (B) Arachno  
 (C) Closo (D) Octahedral
- 15) Based on Wade's rules of electron counting, structure of carborane,  $CB_8H_{14}$ , is expected to be: (UOHYD MSC 2015)  
 [A] closo [B] nido  
 [C] arachno [D] galacto
- 16) Using Wade's rule predict the structure of  $B_9H_{14}^-$ . (UOHYD PHD 2010)  
 (A) closo (B) nido (C) arachno (D) scorpionato
- 17) Using Wade's rule predict the structure of  $Os_5(CO)_{16}$   
 (A) square pyramid (B) trigonal bipyramid  
 (C) capped tetrahedron (D) butterfly shaped
- 18) The cluster having arachano type structure is: (CSIR NET JUNE 2012)  
 A)  $[Ir_4(CO)_{12}]$  B)  $[Os_3(CO)_{12}]$  C)  $[Os_5(CO)_{16}]$  D)  $[Rh_6(CO)_{16}]$

- 19) The predicted structure of  $SB_9H_{11}$ , according to Wade's rules is:  
 A) Closo                      B) Nido                      C) Arachno                      D) Klado
- 20) Structure of a carborane with formula,  $C_2B_4H_8$  is formally derived from:  
 A) Closo-borane                      B) Nido-borane                      (CSIR NET DEC 2012)  
 C) Arachno-borane                      D) Conjuncto-borane
- 21) The total valence electron count and the structure type adopted by the complex  $[Fe_5(CO)_{15}C]$  respectively, are:  
 (CSIR NET JUNE 2014)  
 1) 74 & nido                      2) 60 & closo                      3) 84 & arachno                      4) 84 & nido
- 22) Addition of two electrons to the bismuth cluster  $Bi_5^{3+}$  results in a change of structure type from:  
 (CSIR NET JUNE 2017)  
 1) closo to nido                      3) nido to arachno  
 2) closo to arachno                      4) arachno to hypho
- 23) An example of nido-borane from the following is:                      (GATE 2014)  
 (A)  $B_4H_{10}$                       (B)  $B_6H_{10}$                       (C)  $B_6H_{12}$                       (D)  $B_8H_{14}$
- 24) According to polyhedral electron count rule, the structure of  $Rh_6(CO)_{16}$  is:                      (GATE 2013)  
 (A) closo                      (B) nido                      (C) arachno                      (D) hypho
- 25) The correct classification of  $[B_5H_5]^{2-}$ ,  $B_5H_9$  and  $B_5H_{11}$  respectively is:                      (GATE 2007)  
 a) closo, arachno, nido                      b) arachno, closo, nido  
 c) closo, nido, arachno                      d) nido, arachno, closo
- 26) Which of the following has a nido structure?                      (KERALA SET JUNE 2016)  
 A)  $Ir_4(CO)_{12}$                       B)  $Fe_4(CO)_{15}$                       C)  $Os_5(CO)_{16}$                       D)  $Rh_6(CO)_{16}$
- 27) The carborane  $C_2B_4H_6$  has the structure:                      (KERALA SET FEB 2017)  
 A) Closo – tetrahedron                      B) Nido – trigonalbipyramid  
 C) Closo – octahedron                      D) Arachno - icosahedron
- 28) Identify the following boranes with their class of boranes :                      (MAHARASHTRA SET FEB 2013)  
 (a) closo                      (i)  $B_6H_{12}$   
 (b) nido                      (ii)  $(B_6H_6)^{2-}$   
 (c) arachno                      (iii)  $B_6H_{10}$   
 (A) (a)—(iii), (b)—(i), (c)—(ii)  
 (B) (a)—(i), (b)—(iii), (c)—(ii)  
 (C) (a)—(ii), (b)—(i), (c)—(iii)

(D) (a)—(ii), (b)—(iii), (c)—(i)

- 29) Find out the correct statement(s): (TRB 2017)  
 (A) Decaborane(14) is considered as  $B_{12}H_{12}$  icosahedra frame work from which B1 and B6 have been removed  
 (B) Hexaborane(10) is not a pentagonal prism  
 (C) Icosahedron of  $[B_{12}H_{12}]^{2-}$  is merely the upper limit of a series of deltahedra  $[B_nH_n]^{2-}$   
 (D) If all the vertices of deltahedron are occupied the structure is called nido

Codes:

- (a) B and D                      (b) A and C                      (c) B and C                      (d) D only

- 30) Using total valence electron counting and polyhedral electron counting, the structures of  $Os_5(CO)_{16}$  and  $Os_5(CO)_{15}C$ , respectively are: (UOHYD PHD)

- (A) Closo and nido                      (B) Closo and arachno  
 (C) Nido and arachno                      (D) Nido and closo

- 31) The number of 'framework electron pairs' present borane cluster  $[B_{12}H_{12}]^{2-}$  is: (GATE 2010)  
 a) 10                      b) 11                      c) 12                      d) 13

- 32) The numbers of skeletal electrons present in the compounds  $C_2B_3H_5$ ,  $C_2B_4H_6$ , and  $B_5H_9$  are, respectively, (CSIR NET JUNE 2016)

- 1) 10, 12 and 12                      2) 12, 14 and 14  
 3) 10, 12 and 14                      4) 12, 14 and 12

- 33) The number of bonding molecular orbitals and the number of available skeletal electrons in  $[B_6H_6]^{2-}$ , respectively, are: (CSIR NET JUNE 2017)

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

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**MAXWELL'S RELATIONS**

Following are the four important Maxwell's relations derived from the corresponding thermodynamic equations.

**Thermodynamic equations**                      **Maxwell's relations**

$$dU = TdS - PdV \quad \Rightarrow \quad \left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$

$$dF = -SdT - PdV \quad \Rightarrow \quad \left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

$$dH = TdS + VdP \quad \Rightarrow \quad \left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$$

$$dG = -SdT + VdP \quad \Rightarrow \quad -\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$$

### Euler's reciprocity relation

Let 'f' is a thermodynamic state function that depends on natural variables like  $x_1$  and  $x_2$ , then mathematically we can express this as:

$$\text{i.e. } f = f(x_1, x_2)$$

Since a state function is an exact differential, we can also write,

$$df = \left(\frac{\partial f}{\partial x_1}\right)_{x_2} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_1} dx_2$$

Let,

$$y_1 = \left(\frac{\partial f}{\partial x_1}\right)_{x_2} \quad \& \quad y_2 = \left(\frac{\partial f}{\partial x_2}\right)_{x_1}$$

We can rewrite the equation as:

$$df = y_1 dx_1 + y_2 dx_2 \quad \text{----- (1)}$$

For above two dimensional function, according to Euler's reciprocity relation, we can write:

$$\left(\frac{\delta y_1}{\delta x_2}\right)_{x_1} = \left(\frac{\delta y_2}{\delta x_1}\right)_{x_2}$$

Above is true only when 'f' is an exact differential (i.e. state function).

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## DERIVATION OF MAXWELL'S RELATIONS

### 1st Maxwell's relation

Let us consider the first thermodynamic equation for a state function, U (internal energy) which depends on two natural variables S and V, i.e.

$$dU = TdS - PdV$$

This is in the form of:

$$df = y_1 dx_1 + y_2 dx_2$$

Then by applying Euler's relation, we can write:

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$

It is first Maxwell's relation.

For a clear understanding, I am writing the relations once again.

$$df = y_1 dx_1 + y_2 dx_2 \Rightarrow \left(\frac{\delta y_1}{\delta x_2}\right)_{x_1} = \left(\frac{\delta y_2}{\delta x_1}\right)_{x_2}$$

$$dU = TdS - PdV \Rightarrow \left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$

### Extra information

Since

$$y_1 = \left(\frac{\partial f}{\partial x_1}\right)_{x_2} \quad \& \quad y_2 = \left(\frac{\partial f}{\partial x_2}\right)_{x_1}$$

We can also write:

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \& \quad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

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Note: However, above two relations are **NOT** Maxwell's relations.

### 2nd Maxwell's relation

Now consider the equation for Helmholtz free energy, F. It is also a state function that can be expressed in terms of natural variables T and V.

$$dF = -SdT - PdV$$

Then by applying Euler's relation, we can write:

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

It is the second Maxwell's relation.

For a clear understanding.....

$$df = y_1 dx_1 + y_2 dx_2 \quad \Rightarrow \quad \left(\frac{\delta y_1}{\delta x_2}\right)_{x_1} = \left(\frac{\delta y_2}{\delta x_1}\right)_{x_2}$$

$$dF = -SdT - PdV \quad \Rightarrow \quad \left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

### Extra information

Since

$$y_1 = \left(\frac{\partial f}{\partial x_1}\right)_{x_2} \quad \& \quad y_2 = \left(\frac{\partial f}{\partial x_2}\right)_{x_1}$$

we can also write:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \& \quad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

Note: Again, above two relations are **NOT** Maxwell's relations.

### 3rd Maxwell's relation

From the following equation for another state function, H (enthalpy) expressed in two natural variables S and P;

$$dH = TdS + VdP$$

We can write the third Maxwell's relation

$$\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$$

Compare and justify yourself.

$$df = y_1 dx_1 + y_2 dx_2 \quad \Rightarrow \quad \left(\frac{\delta y_1}{\delta x_2}\right)_{x_1} = \left(\frac{\delta y_2}{\delta x_1}\right)_{x_2}$$

$$dH = TdS + VdP \quad \Rightarrow \quad \left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$$

#### Extra information

We can also write:

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad \& \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

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#### 4th Maxwell's relation

The thermodynamic relation for Gibbs free energy,  $G$  can be expressed using two natural variables  $T$  and  $P$ ;

$$dG = -SdT + VdP$$

By applying Euler's relation, we can write the following Maxwell's relation

$$-\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$$

Compare and justify yourself.

$$df = y_1 dx_1 + y_2 dx_2 \quad \Rightarrow \quad \left(\frac{\delta y_1}{\delta x_2}\right)_{x_1} = \left(\frac{\delta y_2}{\delta x_1}\right)_{x_2}$$

$$dG = -SdT + VdP \quad \Rightarrow \quad -\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$$

#### Extra information

We can also write:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \& \quad V = \left(\frac{\partial G}{\partial P}\right)_T$$

*"Worrying is a waste of time. It does not change anything.  
It messes with your mind and steals your happiness."*

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## PRACTICE MULTIPLE CHOICE QUESTIONS

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1) Indicate which one of the following relations is NOT correct. (CSIR NET JUNE 2012)

$$1) \left( \frac{\delta T}{\delta V} \right)_S = - \left( \frac{\delta P}{\delta S} \right)_V \quad 2) \left( \frac{\delta T}{\delta P} \right)_S = - \left( \frac{\delta V}{\delta S} \right)_P$$

$$3) \left( \frac{\delta S}{\delta V} \right)_T = \left( \frac{\delta P}{\delta T} \right)_V \quad 4) - \left( \frac{\delta S}{\delta P} \right)_T = \left( \frac{\delta V}{\delta T} \right)_P$$

2) The correct thermodynamics relation among the following is: (CSIR NET DEC 2013)

$$1) \left( \frac{\partial U}{\partial V} \right)_S = -P \quad 2) \left( \frac{\partial H}{\partial V} \right)_S = -P$$

$$3) \left( \frac{\partial G}{\partial V} \right)_S = -P \quad 4) \left( \frac{\partial A}{\partial V} \right)_S = -S$$

3) For a process in a closed system, temperature is equal to: (CSIR NET DEC 2014)

$$1) \left( \frac{\partial H}{\partial P} \right)_S \quad 2) \left( \frac{\partial A}{\partial V} \right)_T$$

$$3) \left( \frac{\partial G}{\partial P} \right)_T \quad 4) \left( \frac{\partial H}{\partial S} \right)_P$$

4) The exact differential  $df$  of a state function  $f(x,y)$ , among the following is: (CSIR NET DEC 2014)

$$1) xdy \quad 2) dx - \frac{x}{y} dy \quad 3) ydx - xdy \quad 4) \frac{1}{y} dx - \frac{x}{y^2} dy$$

5) Match the following Maxwell's relations: (PG TRB 2017)

A)  $dU = TdS - PdV$       i)  $\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$

B)  $dH = TdS + VdP$       ii)  $-\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$

C)  $dF = -SdT - PdV$       iii)  $\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$

D)  $dG = -SdT + VdP$       iv)  $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$

- |    | (A)   | (B)   | (C)   | (D)  |
|----|-------|-------|-------|------|
| 1) | (iii) | (i)   | (iv)  | (ii) |
| 2) | (i)   | (iii) | (iv)  | (ii) |
| 3) | (iii) | (ii)  | (i)   | (iv) |
| 4) | (ii)  | (iv)  | (iii) | (i)  |

6) In one of the Maxwell's relations,  $\left(\frac{\delta S}{\delta P}\right)_T$  equals to: (TAMILNADU SET 2017)

- 1)  $\left(\frac{\delta V}{\delta T}\right)_P$       2)  $\left(\frac{\delta V}{\delta T}\right)_V$       3)  $-\left(\frac{\delta V}{\delta T}\right)_P$       4)  $\left(\frac{\delta P}{\delta T}\right)_V$

7) Using the fundamental equation  $dF = -SdT - PdV$ , the Maxwell relation is:

- 1)  $\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$       2)  $-\left(\frac{\delta S}{\delta P}\right)_T = \left(\frac{\delta V}{\delta T}\right)_P$
- 3)  $\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$       4)  $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$

8) The Maxwell's relation  $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$  results from: (UOHYD PHD 2017)

- A)  $dU = dQ - dW$       B)  $dH = dU + PdV + VdP$
- C)  $dA = dU - TdS - SdT$       D)  $dG = dH - TdS - SdT$

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## SELECTED & IMPORTANT TOPICS

### AROMATICITY STUDY MATERIAL

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#### WHAT IS AROMATICITY?

Aromaticity refers to unexpected high stability and resistance to electrophilic addition reactions shown by a few cyclic unsaturated compounds. They undergo electrophilic substitution rather than addition.

Benzene is the best example. It does not undergo addition reactions. For example, with  $\text{Br}_2$ , no addition will take place. However, it forms an electrophilic substitution product, bromobenzene with  $\text{Br}_2$  in presence of Lewi's acid.

The compounds can be divided into aromatic, anti aromatic and non aromatic based on following characteristics. Let us have a bird eye view first followed by illustrations.

#### AROMATIC COMPOUNDS

- i) The molecule must be **cyclic and planar** (more or less).
- ii) According to **Huckel's rule**, there should be  $(4n+2)\pi$  electrons that can be delocalized along the periphery of the ring in a closed loop.
  - \* The  $\pi$ -electrons may be  $\pi$ -bonding electrons or lone pairs in the orbitals perpendicular to the aromatic ring system.
  - \* The carbons or heteroatoms that are part of aromatic ring system must be  $sp^2$  or  $sp$  hybridized. Any  $sp^3$  hybridized atom in the middle breaks the closed loop.
- iv) Aromatic compounds are **diamagnetic** since they contain paired electrons in the molecular orbitals.
  - \* In a strong magnetic field, a diamagnetic ring current or diatropic ring current is produced by the  $\pi$ -electrons of the aromatic ring that creates its own magnetic field. As a result, the protons outside the aromatic ring are deshielded and appear at down field in  $^1\text{H}$ -NMR spectrum. The protons inside the aromatic ring are shielded and appear at up field.

v) These are highly stable compounds with extremely high resonance energy values.

**Note:**

\* Strictly speaking, Huckel's rule was proposed for monocyclic compounds only. However, we can extend the idea to other systems too.

**Huckel's numbers:** Since 'n' can have values 0,1,2,3,....., the cyclic planar system with 2, 6, 10, 14, 18..... delocalized  $\pi$  electrons (in a cyclic manner) is said to be aromatic.

**ANTI-AROMATIC COMPOUNDS**

i) The molecule must be **cyclic and planar** (more or less).

ii) There should be  **$4n\pi$**  electrons that would be delocalized along the periphery of the ring in a closed loop.

\* These molecules also contain continuous atoms which are  $sp^2$  or  $sp$  hybridized.

iii) These are **paramagnetic** since there are unpaired electrons in the MO's.

\* Due to paramagnetic or paratropic ring current the protons outside the anti-aromatic ring are shielded and appear at up field, whereas those inside the ring appear at down field.

iv) These are **highly unstable** systems.

**Note:** Thus the cyclic planar system with 4, 8, 12, 16..... delocalized  $\pi$  electrons is said to be anti-aromatic.

**NON-AROMATIC COMPOUNDS**

i) They may contain  $(4n+2)\pi$  or  $4n\pi$  electrons which may or may not be in conjugation. These  $\pi$ -electrons **may or may not be in a closed loop**.

ii) They may be **cyclic or non-cyclic**.

ii) However, these are **non planar** and hence neither aromatic nor anti-aromatic.

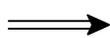
iii) These are moderately stable.

**Note:** Any molecule that is neither aromatic nor anti-aromatic is said to be non-aromatic.

**ILLUSTRATIONS**

*"The more storage you have, the more stuff you accumulate."*

**1) Benzene**



Cyclic & Planar

$6\pi$  electrons (A Huckel number)

**Aromatic**

## 2) Naphthalene



Cyclic & Planar

$10\pi$  electrons (A Huckel number)

**Aromatic**

**Note:** Huckel's rule is applicable to monocyclic systems only. However, naphthalene is bicyclic. In this case, we look at the  $\pi$ -electrons on the periphery of the ring. One should not confuse with the position of double bond. Only the atoms involved in the closed loop with  $\pi$ -electrons are important in arriving at aromatic nature.

## 3) Cyclopropene



Cyclic & Planar

$2\pi$  electrons -  $(4n+2)\pi$  electrons.....but see below

**Non-aromatic** (since there is no closed loop of delocalized  $\pi$ -electrons)

## 4) Cyclopropenyl cation



Cyclic & Planar

$2\pi$  electrons -  $(4n+2)\pi$  system

**Aromatic**

## 5) Cyclopropenyl anion



Cyclic & Planar

$4\pi$  electrons -  $(4n)\pi$  system

**Anti-aromatic**

## 6) Cyclobutadiene



Cyclic & Planar

$4\pi$  electrons (Not a Huckel number)

**Anti-aromatic**

**Note:** It is less stable than non aromatic 1,3-butadiene. To avoid anti-aromaticity and to achieve stability, this molecule tends to adopt unsymmetric rectangular shape in which the bond lengths of double and single bonds differ markedly to prevent overlapping of p-orbitals.

## 7) Cyclopentadiene



Cyclic & Planar

$4\pi$  electrons -  $(4n)\pi$  electrons.....but see below

**Non-aromatic** (since there is no closed loop of delocalized  $\pi$ -electrons)

## 8) Cyclopentadienyl anion



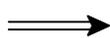
Cyclic &amp; Planar

 $6\pi$  electrons (Huckel number)**Aromatic**

Hence cyclopentadiene is acidic and tends to lose a proton easily to form aromatic cyclopentadienyl anion

**9) Cyclopentadienyl cation**

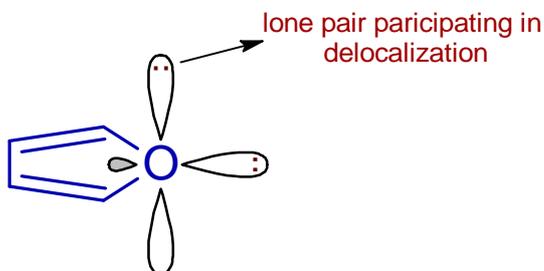
Cyclic &amp; Planar

 $4\pi$  electrons -  $(4n)\pi$  system**Anti-aromatic****10) Furan**

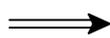
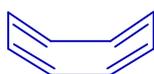
Cyclic &amp; Planar

 $6\pi$  electrons (A Huckel number)**Aromatic**

There are two lone pairs on oxygen. One is in the plane of the ring and the second one is perpendicular. The latter is participating in delocalization and hence contributes to aromaticity. Thus the hybridization on oxygen should be  $sp^2$ .

**11) Cyclooctatetraene (COT)**

or



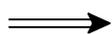
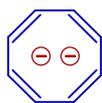
Cyclic &amp; Non-planar

 $8\pi$  electrons -  $(4n)\pi$  system**Non-aromatic**

Even though there are  $8\pi$  electrons (a non-Huckel number), this compound is non-aromatic since the molecule adopts non planar structure (Tub shape). It is a [8]-annulene.

If it is planar, it will be anti-aromatic and becomes unstable. To avoid this, the molecules adopts tub shape.

**12) Dianion of COT**



Cyclic &amp; planar

 $10\pi$  electrons -  $(4n+2)\pi$  system**Aromatic**

It adopts planar shape to get more stability.

### 13) Cyclodecapentaene



Cyclic &amp; Non-planar

 $10\pi$  electrons -  $(4n+2)\pi$  number**Non-aromatic** (since it is non planar)

It is a [10]-annulene. The H's on 1 & 6 positions (see below) prevent the molecule to be planar. Hence non-aromatic inspite of presence of  $10\pi$  electrons. Note that there are two trans double bonds.



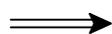
There is another form with all cis double bonds as shown below. It is also non-planar and hence non-aromatic.



**14) 1,6-Methanonaphthalene** - is also a [10]annulene. It is aromatic since the transannular methylene bridge forces the system to be planar and hence it is aromatic.



### 15) Tropylium cation



Cyclic &amp; Planar

 $6\pi$  electrons -  $(4n+2)\pi$  system**Aromatic**

**Note:** Benzyl cation tends to isomerize to tropylium cation.

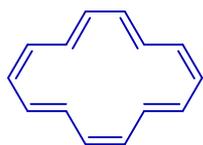
### 16) Cycloheptatriene



Cyclic &amp; Non-Planar

 $6\pi$  electrons -  $(4n+2)\pi$  electrons.....but no closed loop of delocalized  $\pi$ -electrons**Non-aromatic**

**17) [14]-Annulene** -  $14\pi$  electrons. Only the planar conformers are aromatic.



Cyclic &amp; Planar

 $14\pi$  electrons -  $(4n+2)\pi$  system

Aromatic

18) In the following molecule, there are  $14\pi$ -electrons delocalized in a closed loop of parallel p-orbitals along the periphery.



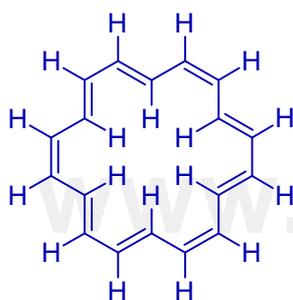
Cyclic &amp; Planar

 $14\pi$  electrons -  $(4n+2)\pi$  system - on the periphery in closed loop

Aromatic

19) [18]-Annulene - is also planar and hence aromatic. The cavity in [18]-annulene is sufficiently large and hence the steric interaction involving internal hydrogens is at minimum. The molecule is nearly planar as it is free of any significant angle strain, and thus is aromatic.

It is diatropic molecule. The outer protons resonate at 9.28 ppm, whereas the inner protons at -3 ppm.



[18]-annulene

Cyclic &amp; Planar

 $18\pi$  electrons -  $(4n+2)\pi$  system

Aromatic

**Note:** The dianion of [18]-annulene is anti-aromatic and paratropic. The inner protons are strongly deshielded at 20.8 ppm and 29.5 ppm and the outer protons are shielded at -1.1 ppm.

20) [12]-Annulene - It has  $12\pi$ -electrons and expected to be anti-aromatic. However, this molecule has the flexibility to become non-planar and hence show non-aromaticity.



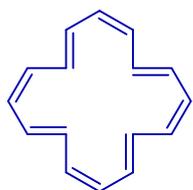
Cyclic &amp; Non-planar

 $12\pi$  electrons -  $(4n)\pi$  system

Non-aromatic (flexibility to exists in non planar shape)

Its dianion is aromatic and stable.

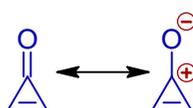
21) [16]-Annulene - Just like [12]-annulene, it is also non-aromatic instead of anti-aromatic.



Cyclic &amp; Non-planar

 $16\pi$  electrons -  $(4n)\pi$  system**Non-aromatic** (flexibility to exists in non planar shape)

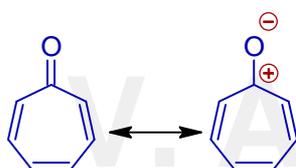
**22) Cyclopropenone** - Due to polarization of C=O group, the carbonyl carbon carries partial positive charge. This makes cyclopropenone aromatic.



Cyclic &amp; planar

 $2\pi$  electrons -  $(4n+2)\pi$  system**Aromatic** (due to polarization of C=O group)

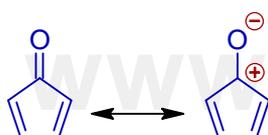
**23) Cycloheptatrienone (Tropone)**



Cyclic &amp; planar

 $6\pi$  electrons -  $(4n+2)\pi$  system**Aromatic** (due to polarization of C=O group)

**24) Cyclopentadienone**

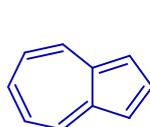


Cyclic &amp; planar

 $4\pi$  electrons -  $(4n)\pi$  system**Anti-aromatic** (due to polarization of C=O group)

It undergoes Diels-Alder dimerization easily so as to avoid anit-aromatic nature.

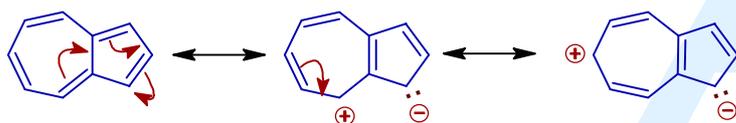
**25) Azulene** - is a non benzenoid aromatic compound (isomer of naphthalene) showing dipole moment. It is obtained from fusion of cyclopentadiene and cycloheptatriene rings.



Cyclic &amp; planar

 $10\pi$  electrons -  $(4n+2)\pi$  system**Aromatic**

To account for dipole moment, it can also be viewed as the fusion of a  $6\pi$ -electron cyclopentadienyl anion and a  $6\pi$ -electron tropylium cation.

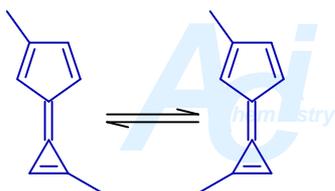


**26) Calicene (Triapentafulvalene) -**

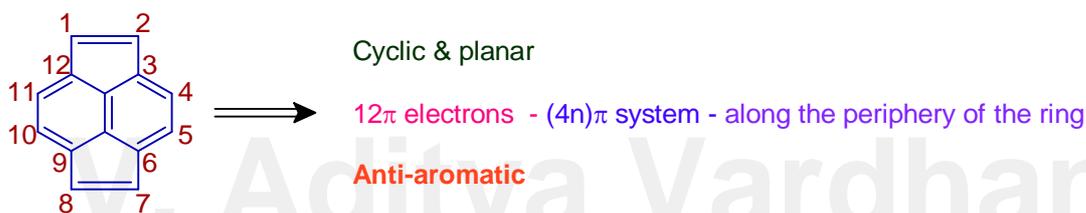


Fulvalenes contain two rings connected through a common exo-cyclic double bond. **Calicine** is a fulvalene that exists in a zwitterionic form with two aromatic rings i.e, a cyclopentadienyl anion ( $6\pi$  electrons) and a cyclopropenyl cation ( $2\pi$  electrons).

Thus there is free rotation about the bond connecting two rings. Because of this following cis and trans isomeric structures exist in equilibrium.



27)

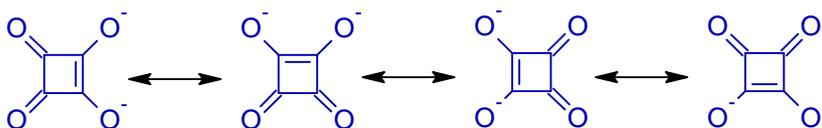


We should NOT take into account of the the  $\pi$ -electrons of middle double bond to decide aromaticity as they are not part of the closed loop.

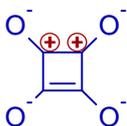
28)



29) **Dianion of squaric acid (squarate anion)**- is resonance stabilized as shown below:

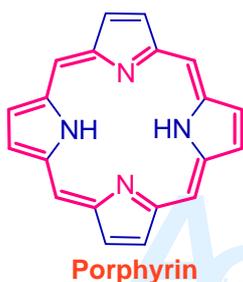


and can also be represented by following, in which all the oxygens have negative charges and the ring has dipositive charge.



Thus, it can be considered as aromatic since there are  $2\pi$ -electrons which can be delocalized.

30) **Porphyrin** - is a rigid planar aromatic macrocyclic compound with four pyrrole rings. Its aromaticity is described in terms of the [18]annulene model (see below for the ring in pink color). Thus porphyrin is viewed as a bridged diaza[18]annulene.



The peripheral protons show downfield shifts whereas the inner hydrogens on N atoms appear at upfields in  $^1\text{H-NMR}$  spectrum.

*“To live on a day-to-day basis is insufficient for human beings;  
we need to transcend, transport and escape”*

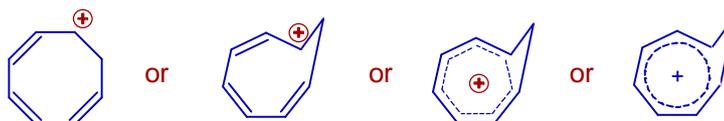
### HOMOAROMATICITY

Homoaromaticity is a special case of aromaticity. It refers to formation of a closed loop of delocalized  $(4n+2)\pi$  electrons by bypassing one or more saturated atoms ( $\text{sp}^3$  hybridized) in a ring.

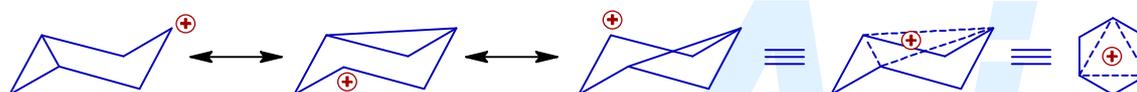
In these systems, the  $\text{sp}^3$  atoms interrupt the continuous overlap of p-orbitals that rules out aromaticity. However, these molecules/ions show considerable thermodynamic stability since they maintain continuous overlap of p-orbitals in a closed loop by avoiding saturated atoms.

### ILLUSTRATIONS

1) **Homotropylium cation** is homoaromatic. It has one  $\text{sp}^3$  hybrid carbon that interrupts continuous overlapping of p-orbitals. However, this atom is bypassed and a continuous ring of  $6\pi$ -electrons is formed that gives aromatic nature to this ion.



2) **bicyclo[3.1.0]hexyl cation (or) tris-homocyclopropenyl cation**



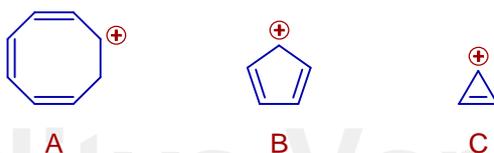
In this ion, the aromatic ring with  $2\pi$  electrons is bypassing three  $\text{sp}^3$  carbons.

**Note:** The ionic aromatic compounds are also termed as **quasi-aromatic** compounds.

## PRACTICE QUESTIONS

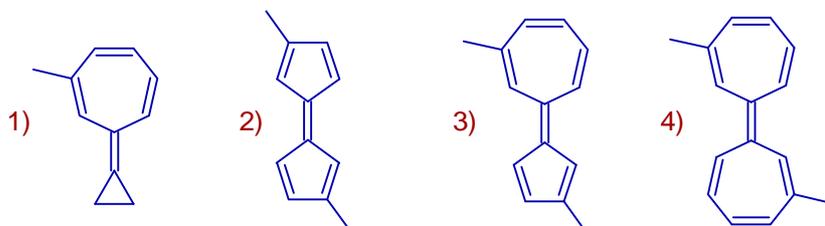
Keys/Solutions along with extra problems (updates) are available at <http://www.adichemistry.com/csir-net/chemistry/key.html>

1) Among the carbocations given below: (CSIR NET JUNE 2011) (CHATTISGARH SET 2016)



- 1) A is homoaromatic, B is antiaromatic and C is aromatic.
- 2) A is aromatic, B is antiaromatic and C is homoaromatic.
- 3) A is antiaromatic, B is aromatic and C is harmoaromatic.
- 4) A is homoaromatic, B is aromatic and C is antiaromatic.

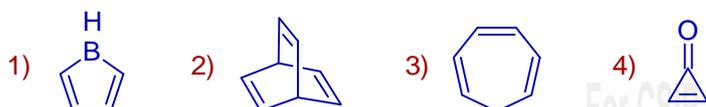
2) Amongst the following, the compound which has the lowest energy barrier for the cis-trans isomerisation is: (CSIR NET DEC 2013)



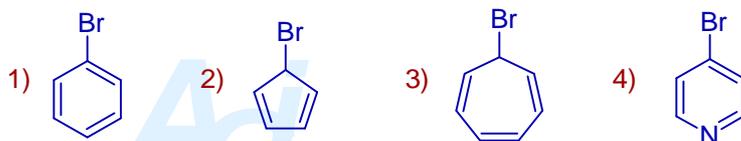
3) Though cyclobutadiene ( $C_4H_4$ ) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because: (CSIR NET JUN 2013)

- 1) it engages in long-range interaction with transition metals.
- 2) it gains stability due to formation of  $C_4H_4^{2-}$  on binding to transition metals.
- 3) its polymerization ability reduces in presence of transition metal.
- 4) it becomes stable in presence of transition metals due to formation of  $C_4H_4^{2+}$ .

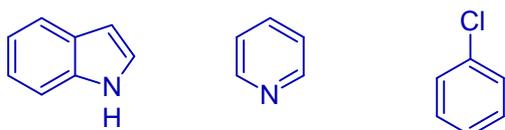
4) The compound that is anti aromatic is: (CSIR NET DEC 2014)



5) The compound that gives precipitate on warming with aqueous  $\text{AgNO}_3$  is: (CSIR NET JUNE 2015)



7) The correct order for the rates of electrophilic aromatic substitution of the following compounds is:



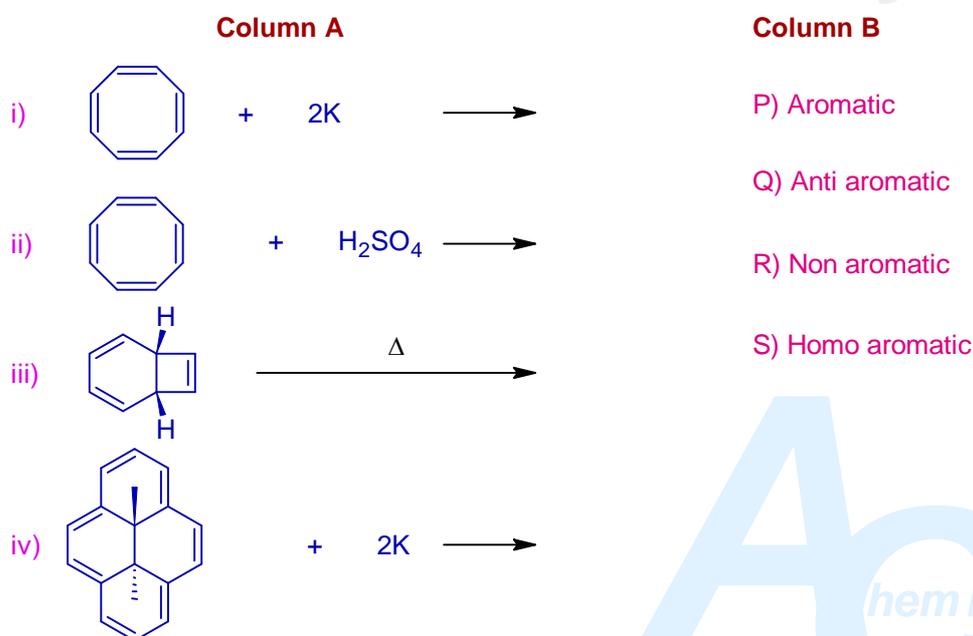
(CSIR NET JUNE 2014)

- 1) I > II > III      2) II > I > III      3) III > II > I      4) I > III > II

**Answer: 4**

**Explanation:** Electron withdrawing groups decrease the electron density on the ring. However, in the first one the N atom is in one ring can donate electron pair and hence is more reactive towards electrophiles.

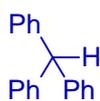
8) Correct match for the products of the reactions in Column A with the properties in Column B is:



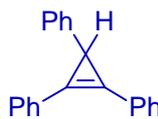
- 1) i - P, ii - S, iii - R, iv - Q  
3) i - Q, ii - R, iii - S, iv - P

- 2) i - P, ii - R, iii - Q, iv - S  
4) i - S, ii - Q, iii - R, iv - P

9) The correct statements are about the reaction of X and Y with  $\text{NaNH}_2$  are:



X



Y

- A. X reacts faster than Y  
 B. Y reacts faster than X  
 C. X and Y behave as Lewis acids  
 D. X is stronger Bronsted acid than Y

- 1) A and C      2) A and D      3) B and C      4) B and D

10) The aromaticity of the following heterocycles is in the order (GATE 1998)

- A) thiophene>pyrrole>furan>pyridine      B) furan>pyrrole>thiophene>pyridine  
 C) pyridine>thiophene>pyrrole>furan      D) pyridine>furan>pyrrole>thiophene

11) Which of the following is not an aromatic compound? (GATE 1999)



12) Choose the correct statement about Naphthalene and its isomer Azulene.

- A) Naphthalene has dipole moment and is a polar molecule, whereas its isomer Azulene is non polar.  
 B) Both Naphthalene and Azulene have zero dipole moment.  
 C) Naphthalene has zero dipole moment, whereas Azulene has a dipole moment of 0.8 Debye.  
 D) Naphthalene and Azulene are aromatic polar compounds.

13) The following hydrocarbon has a dipole moment of 0.8 D because: (GATE 2000)



- A) it exists as in which both the rings exhibit aromaticity

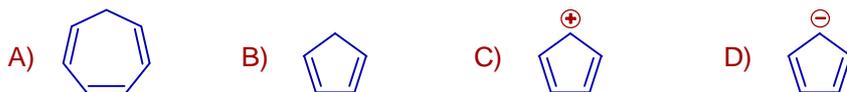
- B) charge separation permits conformational stability

- C) the two rings are of different size  
D) the molecule obeys  $4n + 2$  Huckel rule

14) Among the resonance forms given below, the one which contributes most to the stability of azulene is:



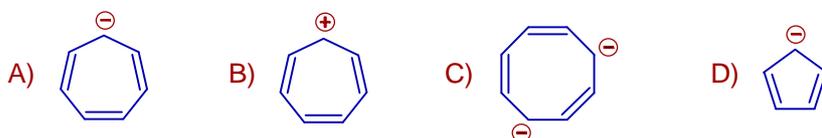
15) The compound that is aromatic, among the choices, is: (GATE 2010 XL)



16) The non-aromatic compound/ion is: (GATE 2012 XL)



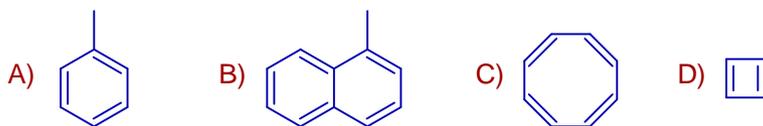
17) The compound that is not aromatic is: (GATE 2008)



18) The compound  is: (GATE 2009)

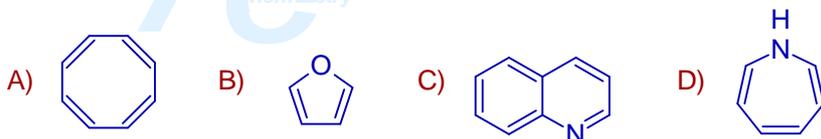
- a) aromatic and has high dipole moment  
b) aromatic and has no dipole moment  
c) non-aromatic and has high dipole moment  
d) anti-aromatic and has no dipole moment

19) Non-aromatic species among the following: (APSET 2012)



20) Non-aromatic compounds among the following:

(APSET 2013)



21) Consider the following statements for [18]-annulene.

(CHATTISGARH SET 2016)

- It is aromatic
- The inner protons resonate at 9.28 in its  $H^1NMR$  spectrum
- There are six protons in the shielded zone

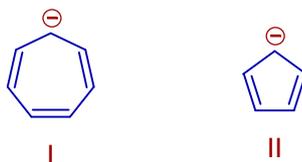
The correct statements are:

- (a), (b) & (c)
- (a) and (b) only
- (b) and (c) only
- (a) and (c) only

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22) Which of the following statement is correct ?

(KARNATAKA SET 2014)



I and II are:

- Both aromatic
- Antiaromatic and aromatic
- Aromatic and antiaromatic
- Both antiaromatic

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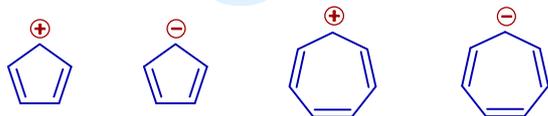
23) Select a pair of aromatic structure from the following:

(KERALA SET 2010)

- (a) cyclopropenyl cation  
 (b) cyclononatetraenyl anion  
 (c) pentalene  
 (d) cyclooctatetraene

A) (b) and (d)      B) (a) and (c)      C) (a) and (b)      D) (c) and (d)

24) Which of the following show aromatic character? (KERALA SET 2011)



I                      II                      III                      IV

A) I and III                      B) II and IV                      C) II and III                      D) I, II, III and IV

25) Among the following the aromatic compound is: (KERALA SET 2011)



A)      B)      C)      D)

26) Which among the following compound is most aromatic? (KERALA SET 2012)

A) Pyrrole                      B) Pyridine                      C) Pyrimidine                      D) Thiophene

27) Tropilium cation is \_\_\_\_\_ (KERALA SET 2012)

A) Antiaromatic      B) Homoaromatic      C) Heteroaromatic      D) Nonaromatic

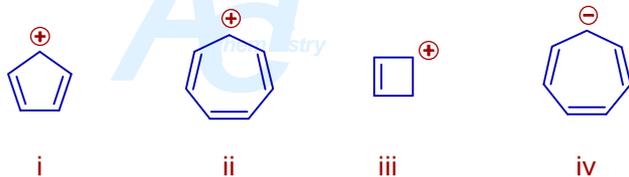
28) The decreasing order of resonance energies (stabilities) of aromatic, anti aromatic and non aromatic compounds is: (KERALA SET 2013)

- A) Aromatic > anti aromatic > non aromatic  
 B) Anti aromatic > aromatic > non aromatic  
 C) Non aromatic > anti aromatic > aromatic  
 D) Aromatic > non aromatic > anti aromatic

29) Which of the following is non-aromatic? (KERALA SET 2013)



30) Which among the following is/are antiaromatic? (KERALA SET 2015)



A) i & ii only      B) ii & iv only      C) i & iv only      D) i, ii & iv only

31) Which among the following is/are antiaromatic? (KERALA SET 2016)



A) i & ii only      B) ii & iii only      C) iv only      D) ii only

32) Which of the following statements is wrong? (KERALA SET 2017)

- A) Benzene, a [6] annulene is aromatic
- B) Cyclobutadiene, a [4] annulene is antiaromatic
- C) Cyclooctatetraene, an [8] annulene is nonaromatic
- D) Cyclodecapentaene, a [10] annulene is aromatic

34) Which of the following is not a criteria for aromaticity? (MAHARASHTRA SET DEC 2013)

- (A) Presence of  $(4n + 2)$  delocalizable electrons
- (B) Diamagnetic character
- (C) Strong shielding-de-shielding pattern as a result of induced ring current
- (D) Paramagnetic character

35) Which of the following compounds is not aromatic in nature? (MAHARASHTRA SET FEB 2013)

- (A) Cyclopentadienyl anion
- (B) Pyrrole
- (C) Fullerene  $C_{60}$
- (D) Azulene

Keys/Solutions along with extra problems (updates) are available at <http://www.adichemistry.com/csir-net/chemistry/key.html>

36) Choose the correct option as indicated in series given below: (MAHARASHTRA SET FEB 2013)

a) Homoaromatic



i



ii



iii

b) Aromatic



i



ii



iii

c) Non-aromatic



i



ii

C<sub>60</sub>

iii

- (A) Homoaromatic-i, Aromatic-ii, Non-aromatic-iii  
 (B) Homoaromatic-ii, Aromatic-iii, Non-aromatic-iii  
 (C) Homoaromatic-ii, Aromatic-ii, Non-aromatic-ii  
 (D) Homoaromatic-ii, Aromatic-ii, Non-aromatic-iii

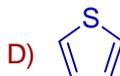
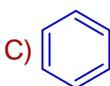
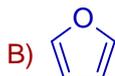
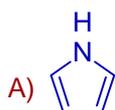
37) Which of the following compound is not aromatic according to Huckel  $4n+2$  rule ?

- 1) Pyridine                      2) Anthracene                      (RAJASTHAN PSC 2016)  
 3) Pyrrole                        4) Cycloheptatriene

38) Huckel's rule states that a conjugated polymethine will be aromatic, if it contains:

- 1)  $(4n+2)\pi$  electrons                      2)  $(2n+2)\pi$  electrons  
 3)  $(4n+4)\pi$  electrons                      4)  $(4n+2)\sigma$  electrons

39) The correct decreasing order of relative resonance energies of following compound is:



(PG TRB 2017)

(a) (C) &gt; (B) &gt; (D) &gt; (A)

(b) (B) &gt; (A) &gt; (C) &gt; (D)

(c) (A) &gt; (B) &gt; (C) &gt; (D)

(d) (C) &gt; (D) &gt; (A) &gt; (B)

40) The correct relative reactivity towards electrophilic aromatic substitution of the following compounds are: (PG TRB 2017)

(A) Benzene (B) Furan (C) Pyrrole (D) thiophene

(a) (A) &gt; (C) &gt; (B) &gt; (D)

(b) (A) &gt; (B) &gt; (C) &gt; (D)

(c) (C) &gt; (B) &gt; (D) &gt; (A)

(d) (C) &gt; (D) &gt; (B) &gt; (A)

41) Which of the following is aromatic?

(TAMILNADU SET 2017)

- 1) 1,3,5,7-tetramethylcyclooctatetraene
- 2) 1,3,5,7-tetramethylcyclooctatetraene cation
- 3) 1,3,5,7-tetramethylcyclooctatetraene anion
- 4) 1,3,5,7-tetramethylcyclooctatetraene dication

42) Which of the following is not aromatic?

(A) Azulene (B) [18]-annulene (C) Cyclopropyl cation (D) Cyclopentadienyl anion

43) Cyclooctatetraene is not aromatic. The most important reason for this is that:

- (a) it has  $4n$  electrons
- (b) it is a planar molecule
- (c) its structure is not that of regular octagon
- (d) its structure cannot be described by more than two canonical forms

(TRB POLYTECHNIC EXAM 2017)

44) Consider the following statements:

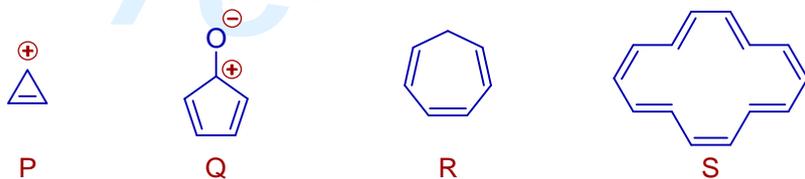
(TRB POLYTECHNIC EXAM 2017)

- (A) Azulene is aromatic
- (B) [10] Annulene is not aromatic
- (C) [10] Annulene is having  $4n\pi$  electrons

Of these statements

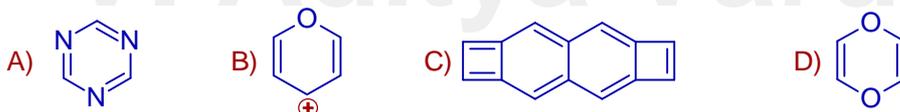
- (a) A, B and C are correct      (b) A and B are correct  
(c) A and C are correct      (d) B and C are correct

45) The species/compounds that are aromatic among the following are: (IIT JAM 2012)

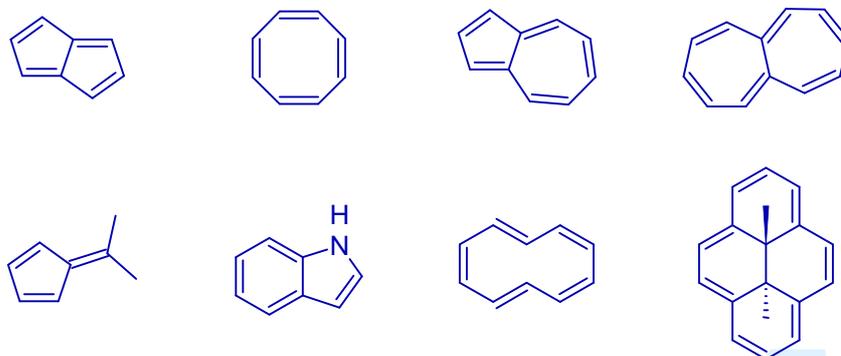


- (A) R and S      (B) P and Q      (C) Q and S      (D) P and S

45) The species/compounds that are aromatic among the following are: (IIT JAM 2015)



46) Among the following, the number of molecules that are aromatic is \_\_\_\_\_. (IIT JAM 2016)



47) Which is least aromatic? (BHU MSC 2010)

- (1) Thiophene      (2) Pyrrole      (3) Furan      (4) Benzene

48) Which of the following is NOT an aromatic compound? (IISC INT PHD 2007)

- (a) cyclopentadiene      (b) benzene      (c) pyridine      (d) cyclopropenium cation

49) Which of the following organic compounds is not aromatic? (IISC INT PHD 2011)

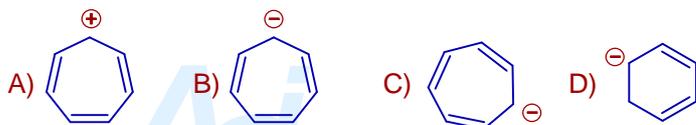
(a) Azulene

(b) naphthalene

(c) furan

(d) cyclopentadienyl cation

50) Which of the following hydrocarbons will exhibit aromatic stabilization? (IISC INT PHD 2012)



Answer: A

51) 1,3,5,7-Cyclononatetraene can be converted to an aromatic substance by: (UOHYD MSC 2013)

(A) hydrogen atom abstraction

(B) hydride abstraction

(C) proton abstraction

(D) H<sub>2</sub> elimination

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