Inspire academy @ Pudukkottai- 622001
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SPINEL & INVERSE SPINEL STRUCTURES

The spinels have the general formula AB_2X_4.
Where:
A^{II} = a divalent cation like Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn
B^{III} = a trivalent cation like Al, Ga, In, Ti, V, Cr, Mn, Fe, Fe, Co, Ni
X = O, S, Se etc.

Structure of Normal Spinels (AB_2O_4): The divalent AII ions occupy the tetrahedral voids, whereas the trivalent BIII ions occupy the octahedral voids in the close packed arrangement of oxide ions.

A normal spinel can be represented as: $(A^{II})^{tet}(B^{III})_2{}^{oct}O_4$
E.g. $MgAl_2O_4$ (known as spinel), Mn_3O_4, $ZnFe_2O_4$, $FeCr_2O_4$ (chromite)

Structures of Inverse spinels ($B(AB)O_4$): The AII ions occupy the octahedral voids, whereas half of B^{III} ions occupy the tetrahedral voids.

Inverse spinels can be represented as: $(B^{III})^{tet}(A^{II}B^{III})^{oct}O_4$
E.g. Fe_3O_4 (ferrite), $CoFe_2O_4$, $NiFe_2O_4$ etc.

The above inverse spinels can also be written as:

$Fe_3O_4 = Fe^{III}(Fe^{II}Fe^{III})O_4$
$CoFe_2O_4 = Fe^{III}(Co^{II}Fe^{III})O_4$
$NiFe_2O_4 = Fe^{III}(Ni^{II}Fe^{III})O_4$

The number of octahedral sites occupied may be ordered or random.
The random occupation leads to defected spinels.

E.g. $NiAl_2O_4$ for which the formula can be written as $(Al_{0.75}Ni_{0.25})^{tet}$ $[Ni_{0.75}Al_{1.25}]^{octa}O_4$.

Another defected spinel is γAl_2O_3

FACTORS AFFECTING THE STRUCTURE OF SPINELS

1) The relative sizes of A and B: In general, the smaller cation prefers to occupy the site of lower coordination i.e., tetrahedral site.

However, in the spinel, $MgAl_2O_4$ itself this factor is outweighed by greater lattice energy of smaller cation, Al^{3+}, which occupies the octahedral site and thus by giving normal spinel structure. Otherwise the "spinel" will have the inverse spinel structure

2) The Madelung constants for the normal and inverse structures: It is observed that the Madelung constants are same for both normal and inverse spinels and hence are not that much important in arriving at the structure.

3) LigandFleld
Stabilization Energies: Applicable whenever there are transition metal ions and is discussed below. The structures of spinels are affected by the relative LFSE values of metal ions.

The ion with more LFSE value in octahedral geometry when compared to the LFSE in tetrahedral geometry tends to occupy octahedral sites.

The difference between the LFSE values in octahedral and tetrahedral geometries is referred to as Octahedral Site Stabilization Energy (OSSE).

"If the B^{III} ion has more CFSE gain in octahedral site than that of A^{II} ion, a normal spinel is expected."

"Whereas an inverse spinel is formed whenever the divalent AII ion has comparatively more CFSE gain in octahedral geometry than the trivalent B^{III} ion."

SOME GENERALIZATIONS REGARDING THE STRUCTURES OF SPINELS

* A normal spinel structure is assumed if both the divalent and the trivalent metals are non transition metals since no CFSE is involved.

* There is a tendency of formation of inverse spinel structure in some cases (not all the cases) which contain transition metal ions. This is because, the transition metal ion may get extra stability (LFSE) in octahedral geometry, prefers octahedral voids over tetrahedral ones.

* The d^0; high spin d^5, d^{10} ions have no preference between tetrahedral and octahedral coordination since the LFSE is zero.

* Usually d^3 & d^8 ions have strongest preference for octahedral geometry.

* Other ions with d^1, d^2, d^4, d^6, d^7, d^9 too have slightly more preference for octahedral symmetry.

* That means, if AII has d^3 or d^8 configuration and the BIII ion has configuration other than these, then the spinel is inverted.

* If the divalent AII is a transition metal (with configurations other than d^0; highspin d^5 & d^{10}) and the BIII ion is a non transition metal, there is a tendency to form inverse spinel. But there are exceptions like $FeAl_2O_4$ which has normal spinel structure.

* Above generalizations are valid for high spin systems as the oxide ion is expected to be a weak field ligand.

For example, Co^{3+} is a low spin system even in presence of oxo ligands due to high charge on the ion.

A^{II}	**A^{III}**	**Structure**
Non transition metal or d^0 or d^5 or d^{10} transition metal	Non transition metal	Spinel structure
Non transition metal or d^0 or d^5 or d^{10} transition metal	A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Spinel structure
A transition metal with d^1 or d^2 or d^3 or d^4 or d^6 or d^7 or d^8 or d^9 configurations	Non transition metal or transition meta with d^0 or d^5 or d^{10} configurations	Inverse spinel
Transition metal with higher CFSE value	Transition metal with lower CFSE value	Inverse spinel

EXAMPLES FOR SPINEL AND INVERSE SPINEL STRUCTURES

1) $MgAl_2O_4$ is a normal spinel since both the divalent and trivalent ions are non transition metal ions. There is no question of CFSE.

2) Mn_3O_4 is a normal spinel since the Mn^{2+} ion is a high spin d5 system with zero LFSE. Whereas, Mn^{3+} ion is a high spin d^4 system with considerable LFSE.

3) Fe_3O_4 is an inverse spinel since the Fe(III) ion is a high spin d^5 system with zero CFSE. Whereas the divalent Fe(II) is a high spin d6 system with more CFSE.

4) $NiFe_2O_4$ is again an inverse spinel since the divalent Ni^{2+} (a d^8 ion) has more CFSE than the trivalent Fe^{3+} (a d^5 ion).

5) $FeCr_2O_4$ is a normal spinel since the divalent Fe^{2+} is a high spin d^6 ion with CFSE = 4 Dq and the trivalent Cr^{3+} is a high spin d^3 ion with CFSE = 12 Dq. Hence Cr^{3+} gets more OSSE while occupying octahedral sites.

6) Co_3O_4 is a normal spinel. Even in the presence of weak field oxo ligands, the Co^{3+} is a low spin d^6 ion with very high CFSE. It is due to high charge on Co^{3+}. Hence all the Co^{3+} ions occupy the octahedral sites.

7) $NiAl_2O_4$ show random or defected inverse spinel. The CFSE of Ni^{II} is greater in octahedral than tetrahedral coordination. But Al^{3+} also has strong preference for octahedral sites due to high lattice energy. This leads to almost complete randomization of all the cations on all the available sites. Its formula can be written as $(Al_{0.75}Ni_{0.25})tet\ [Ni_{0.75}Al_{1.25}]^{octa}O_4$.

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Time 2 hours	PG-TRB 2017 MOCK TEST – CHEMISTRY	Questions 61

1. Match:

	Column I		Column II
A	XeF_6	(i)	Distorted octahedral
B	XeO_3	(ii)	Square planar
C	$XeOF_4$	(iii)	Pyramidal
D	XeF_4	(iv)	Square pyramidal

A B C D
(a) (iv) (iii) (i) (ii)
(b) (iv) (i) (ii) (iii)
(c) (i) (iii) (vi) (ii)
(d) (i) (ii) (iv) (iii)

2. Which of the following is smallest in size?
a) Cl^- b) Na^+ c) Mg^{2+} d) S^{2-}

3. The correct of increasing ionic radii?
a) $BeCl_2<MgCl_2<CaCl_2<BaCl_2$ b) $BeCl_2<MgCl_2<BaCl_2<CaCl_2$
c) $BeCl_2<BaCl_2<MgCl_2<CaCl_2$ d) $BaCl_2<CaCl_2<MgCl_2<BeCl_2$

4. Which of the following is having bent shape?
a) I_3^- b) I_3^+ c) H_2O_2 d) XeO_3

5. The correct order of ionic radii of the species
a) $Na^+<F^-<O^{2-}<N^{3-}$ b) $F^-<O^{2-}<N^{3-}<Na^+$ c) $O^{2-}< Na^+<F^-<N^{3-}$ d) $N^{3-} <Na^+<F^-<O^{2-}$

6. Electronegativities of C, N, Si & P are in the order of
a) P<Si<C<N b) Si<P<N<C c) Si<P<C<N d) P<Si<N<C

7. In which of the following central atom does not use sp^3 hybrid orbitals in its hybrid bonding?
a) NH_2^- b) HCl c) HBr d) HI

8. Which of the following molecules is having highest dipole moment?
a) HF b) I_3^+ c) H_2O_2 d) XeO_3

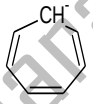
9. Which of the following is a square planar complex?
a) BrF_5 b) $XeOF_4$ c) $[Ni(CN)_4]^{2-}$ d) $[Co(NH_3)_6]^{3+}$

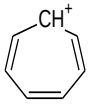
10. The shape of the compounds like ClF, BrF_3, XeF_4 and SF_4?
a) see-saw, square planar, square pyramidal, T-shaped
b) T-shaped, square planar, bent, see-saw
c) T-shaped, square pyramidal, square planar, see-saw
d) square planar, see-saw, T-shaped, square pyramidal

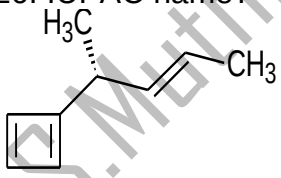
11. Which of the following pair of species have same bond order?
a) NO^+ & CN^+ b) CN^- & NO^+ c) CN^- & CN^+ d) O_2^- & CN^-

12. The ONO bond angle is maximum in
a) NO_3^- b) NO_2^- c) NO_2 d) NO_3^+

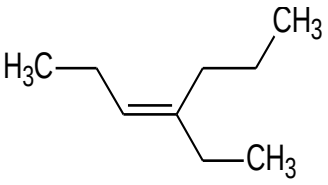
13. In $[Ag(CN)_2]^-$ the no. of π bonds is
a) 2 b) 3 c) 4 d) 6
14. In which of the following bond angle is maximum?
a) NH_3 b) NH_4^+ c) PCl_3 d) SCl_2
15. Mutarotation is characteristic feature of
a) epimers b) enantiomers c) anomers d) ringchain isomers
16. For fructose & glucose the possible optical isomers are
a) 12, 12 b) 8, 16 c) 16, 8 d) 4, 12
17. Which of following is non polar?
a) SO_2 b) CO_2 c) H_2O d) NH_3
18. The Correct order of decreasing bond lengths of CO, CO_2, CO_3^{2-}
a) CO> CO_2> CO_3^{2-} b) CO_3^{2-}>CO_2>CO
c) CO_2>CO>CO_3^{2-} d) CO_2>CO_3^{2-}>CO
19. Which of the following molecules does not show any resonating structure?
a) NH_3 b) CO_3^{2-} c) O_3 d) SO_3
20. The correct sequence of bond length in single bond, double bond and triple bond of C is
a) (C-C) = (C=C) = (C≡C) b) C ≡ C <C= C< C-C
c) C-C < C=C < C≡C d) C =C < C≡C <C-C
21. Arrange the following in increasing order of covalent character – NaCl, $MgCl_2$, $AlCl_3$
a) NaCl<$MgCl_2$<$AlCl_3$ b) $MgCl_2$<NaCl<$AlCl_3$
c) $AlCl_3$<$MgCl_2$<NaCl d) NaCl<$AlCl_3$<$MgCl_2$
22. Which of the following is an aromatic compound
a) Tropilium anion b) Tropilium cation c) Cyclopentadienyl cation d) cyclopropylanion
23. Which of the following is an aromatic species?
a)  b) 

c) 

d) 

24. Ma_3b_3 complex will exhibit the following isomerism
a) cis-trans b) enantiomerism c) fac-meridional d) diastereomers
25. Mabcdef complex will give how many isomers?
a) 15 b) 15d, 15l c) 25 d) 35
26. IUPAC name?


a) 1-cyclobutyl, 2-methyl, but-2-(E)-ene
b) 2-methyl,1-cyclobutyl but-2-(E)-ene
a) 1-cyclo butyl, 2-methyl, but-2-(Z)-ene
a) 2-methyl,1-cyclobutyl but-2-(Z)-ene
27. IUPAC name?



a) trans-4-ethyl hept-3-ene b) E-4-ethyl hept-3-ene
a) Cis-4-ethyl hept-3-ene b) Z-4-ethyl hept-3-ene

28. What is the oxidation state of the Co in $[Co(NH_3)_4(NO_2)_2]^+$?
a) +3 b) +2 c) +1 d) +5

29. What is the density of the ligand 1,10-phenanthroline?
a) 2 b) 1 c) 3 d) 4

30. How many geometrical isomer(s) is/are possible for $[Pt(NH_3)_3Cl]^{+1}$?
a) 1 b) 2 c) 3 d) 0

31. How many geometrical isomer(s) is/are possible for $[Pt(NH_3)Cl_5]^{-1}$?
a) 1 b) 0 c) 2 d) 4

32. How many geometrical isomer(s) is/are possible for $[Pt(NH_3)Cl(NO)_2]$?
a) 1 b) 2 c) 3 d) 4

33. How many geometrical isomer(s) is/are possible for $[Pt(NH_3)_4Cl_{Br}]^{+2}$?
a) 2 b) 4 c) 6 d) 8

34. Which of the following shows geometrical isomerism?
a) $[Mabcd]^{n\pm}$ b) $[Ma_3b]^{n\pm}$ c) $[Ma_2bc]$ d) [Mabcx]

35. Which of the following exhibits ionization isomerism?
a) $[Cr(NH_3)_6]Cl_3$ c) $[M(en)_3]Cl_3$
b) $[M(en)_3Cl_3]$ d) $[M(NH_3)_5Br]SO_4$

36. The pair of $[Co(NH_3)_5SO_4]NO_3$ and $[Co(NH_3)_5NO_3]SO_4$ will exhibit
a) Hydrate isomerism b) linkage isomerism
c) Ionization isomerism d) coordinate isomerism

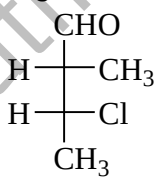
37. Which of the following will have three stereoisomeric forms?

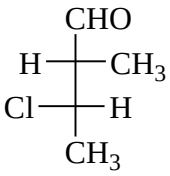
i) $[Cr(NO_3)_3(NH_3)_3]$ ii) $K_3[Co(C_2O_4)_3]$

iii) $K_3[Co(C_2O_4)_2Cl_2]$ iv) $[Co(en)_2ClBr]$

a) (iv) and (iii) b) (iv) and (i) c) (iii) and (ii) d) (i) and (ii)

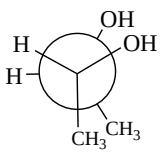
38. The following isomers are

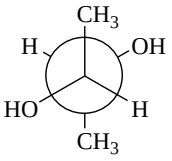


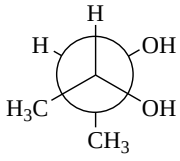


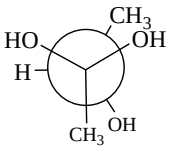
a) enantiomers b) identical c) diastereomers d) meso compound

39. Which of the following does not represent meso form?

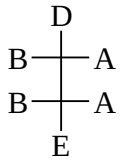
a) 

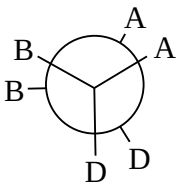
b) 

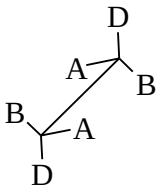
c) 

d) 

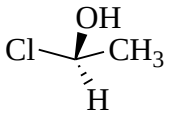
40. Which of the following represents “meso” form?

a) 

b) 

c) 

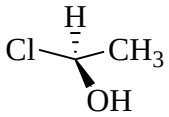
d) all these

112. The stereochemical descriptor of the compound 

is

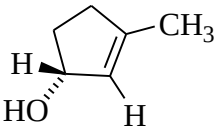
a) R b) S c) D d) L

41. What is the configuration of the following molecule?



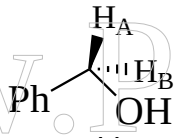
a) R b) S c) L d) D

42. The stereochemical descriptors for the chiral centre and the olefin for the compound



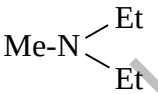
a) S,Z b) R,Z c) S,E d) R,E

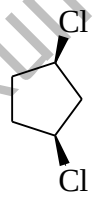
43. In the compound given below, the hydrogen A and B are



a) homotopic b) enantiotopic c) diastereotopic d) isotopic

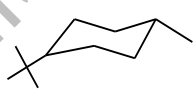
44. Which of the following can show enantiomerism?

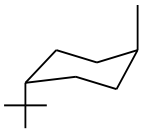
a) 

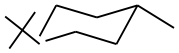
b) 

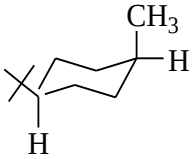
c) both a & b d) none of these

45. The most stable conformer of cis-1-tert-butyl-4-methylcyclohexane is

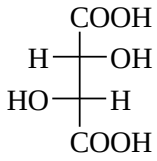
a) 

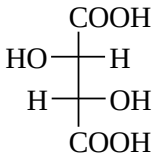
b) 

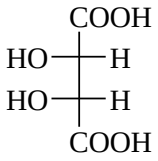
c) 

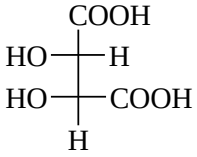
d) 

46. Which of the following represents meso-tartaric acid?

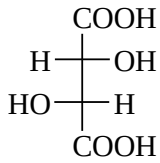
a) 

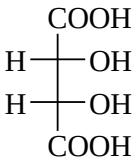
b) 

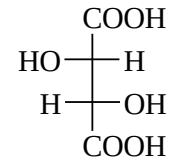
c) 

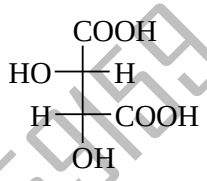
d) 

47. Which of the following represents (S,S)-tartaric acid?

a) 

b) 

c) 

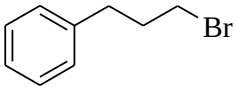
d) 

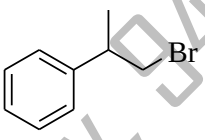
48. The stability of carbonium ions follow the order

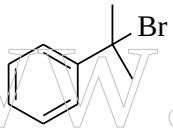
a) $3°>2°>1°>CH_3^+$ b) $3°<2°<1°<CH_3^+$

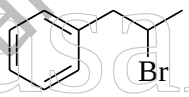
c) $3°>2°>1°<CH_3^+$ d) $3°<2°>1°<CH_3^+$

49. Which of the following alkyl halides would be the most reactive in an S_N2 reaction?

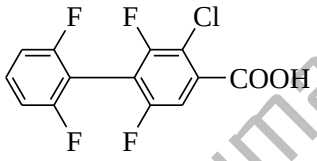
a) 

b) 

c) 

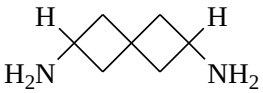
d) 

50. Which of the following compounds exhibit optical isomerism?

a) 

b) $H_2C=C=CH_2$

c) 

d) 

51. Draw MOs and arrange the molecules with their increasing bond lengths & bond energy

O_2^{2-}, O_2^-, N_2, N_2^+, NO^+, NO^-

52. An aromatic compound with 10 electrons in the ring current. According to Huckel's rule for Aromaticity, the value of n is a) 0 b) 1 c) 2 d) 3

53. Which of the following is anti-aromatic?

a) cyclopropene b) cyclopropenyl cation

c) cyclopropenyl anion d) cyclopropenyl radical

54. Which of the following is non-aromatic?

a) 4-annulene b) 6-annulene c) 10-annulene
d) all these

55. Which of the following is not basic?

a) pyrrole b) pyridine c) piperidine d) pyrrolidine

56. Which of the following aromatic compounds have 14 electrons?

a) $C_{10}H_8$ b) $C_{14}H_{10}$ c) $C_{18}H_{12}$ d) all these

57. Which of the following reagents produces a neutral planar simple nucleophile?

a) $HNO_3 + H_2SO_4$ b) $H_2S_2O_7$ c) R-X + $AlCl_3$ d) R-COX + $AlCl_3$

58. Fill the table

Molecule	Bond pairs	Lone pairs	Hybridization	Bond angle	Geometry	Shape
NO_2^+						
ClO_2^-						
I_3^-						
$XeOF_2$						
ClO_3^-						
SbF_5^{2-}						
XeF_6						

59. Find the term state symbols of the following species (centre atoms)
a. $[Fe(CN)_6]^{4-}$ b. $[Fe(CN)_6]3^-$ c. $[Fe(CO)_6]^{2-}$ d. CH_4
60. Find the possible micro states of the following species (centre atoms)
a. $[Fe(CN)_6]^{4-}$ b. $[Fe(CN)_6]3^-$ c. $[Fe(CO)_6]^{2-}$ d. CH_4
61. Find the EAN of the following species
a. [Cr(CO)], b. $Fe(CO)_6$ c. $Fe(CO)_5$, d. $[V(CO)_6]^-$