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PAPER – III

CHEMICAL SCIENCES

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Question Booklet No. 010288

1.

OMR Sheet No.. .....

Subject Code 01 **ROLL No.**

Time Allowed : 150 Minutes **Max. Marks : 150**

No. of pages in this Booklet : **12** No. of Questions : **75**

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01-16

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PAPER-III
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1. What is the eigen value of eigen function $\exp[im\phi]$ when operated by the operator $(-h/2\pi i)\, d^2/d\varphi^2$?

(A) m^2 (B) im^2

(C) $m^2h^2/4\pi^2$ (D) $-m^2h^2/4\pi^2$

2. Which of the following represents the Hamiltonian operator of He atom (in atomic units) ?

(A) $\sum_{i=1}^{2} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{2} \frac{1}{r_i}$

(B) $\sum_{i=1}^{2} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{2} \frac{2}{r_i}$

(C) $\sum_{i=1}^{2} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{2} \frac{2}{r_i} - \sum_{i\neq j} \frac{2}{r_{ij}}$

(D) $\sum_{i=1}^{2} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{2} \frac{2}{r_i} + \sum_{i\neq j} \frac{1}{r_{ij}}$

3. Which of the following is the approximate wave function for H_2 molecule as per LCAO-MO treatment ?

(A) $\psi = N[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)]$

(B) $\psi = N[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1) + 1s_a(1)1s_b(1) + 1s_a(2)1s_b(2)]$

(C) $\psi = N[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1) + 1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)]$

(D) $\psi = N[1s_a(1)1s_b(2)][1s_a(2)1s_b(1)]$

4. Which of the following is NOT the valid approximation in the Simple Huckel Molecular orbital theory applied for conjugated systems ?

(A) $H_{ii} = \alpha$

(B) $H_{ij} = \beta$; i & j being adjacent or non-adjacent

(C) $S_{ii} = 1$

(D) $S_{ij} = 0$; i & j being adjacent or non-adjacent

5. On going from BF_3 to $[BF_4]^-$, the point gr changes from :

(A) D_{3h} to T_d (B) D_{3v} to T_d

(C) D_{3h} to D_{4h} (D) D_{3h} to C_{3v}

6. Which pair of transitions, indicated by n, l, and quantum numbers, of hydrogen atom occur with same value of ΔE ?

(A) (2, 1, 1)→(3, 2, 2) and (3, 2, 2)→(4, 1, 2)

(B) (3, 1, 0)→(5, 2, 1) and (3, 4, 0)→(5, 3, 0)

(C) (2, 1, 1)→(3, 1, 0) and (2, 1, 1)→(4, 1, 0)

(D) (4, 2, 2)→(5, 1, 1) and (4, 1, 1)→(6, 1, 1)

7. Which of the following is TRUE for the partiti function ?

(A) It is independent of temperature and nature molecules.

(B) Its value is infinity when temperature approach infinity and zero when temperature approach absolute zero.

(C) Its value is infinity when temperature approach infinity and unity when temperature approach absolute zero.

(D) Its value is unity when temperature approach infinity and zero when temperature approach absolute zero.

8. Diphenyl Picryl Hydrozyl Radical (DPPH) is us as a standard in which of the following spectroscop techniques ?

(A) NMR spectroscopy

(B) EPR spectroscopy

(C) Mossbaur spectroscopy

(D) IR spectroscopy

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9. The standard cell potential for the reaction

$Cu^{2+}(aq) + Fe^{2+}(aq) + I^{-}(aq) \rightarrow CuI(s) + Fe^{3+}(aq)$

is 0.09 V. Use Nernst equation to calculate the electrochemical potential at 25°C for the cell

$Pt(s) \mid CuI_2$ (aq, 0.01 M) $\mid CuI(s) \parallel FeSO_4$ (aq, 0.01 M), $Fe_2(SO_4)_3$ (aq, 0.02 M) $\mid Pt(s)$

(A) –0.147 V (B) –0.129 V

(C) –0.309 V (D) –0.09 V

10. If the pH of a solution is increased from 0 to 4 at 25°C for the couple MnO_4^-/Mn^{2+}, then the reduction potential of this couple changes by :

(A) –0.18 V (B) 0.18 V

(C) 0.38 V (D) –0.38 V

11. The isomerisation of cis to trans But-2-ene, C_4H_8, follows a Lindemann mechanism. At high pressure, pseudo first order rate constant for the isomerisation is $2 \times 10^5\ s^{-1}$ at 500°C. Given that, at this temperature, collisional activation occurs with an efficiency that is 10^{11} times slower than that of collisional deactivation, the rate constant for final step of the mechanism would be :

(A) $5 \times 10^5\ s^{-1}$ (B) $2 \times 10^{-5}\ s^{-1}$

(C) $2 \times 10^{-16}\ s^{-1}$ (D) $2 \times 10^{-7}\ s^{-1}$

12. A system of non-interacting Fermi particles with Fermi-Energy E_F, has a density of states proportional to $\sqrt{E}$, where E is the energy of a particle. The average energy per particle at 0 K would be :

(A) $1/6\ E_F$ (B) $1/5\ E_F$

(C) $2/5\ E_F$ (D) $3/5\ E_F$

13. A system has two energy levels with the energies E and 2E having degeneracies of 4 and 2 respectively. If there are N non-interacting classical particles in the system being in thermodynamic equilibrium at temperature T, then the fraction of particles in upper level would be :

(A) $\frac{1}{1+e^{-E/kT}}$

(B) $\frac{1}{1+2e^{E/kT}}$

(C) $\frac{1}{2e^{E/kT}+4e^{2E/kT}}$

(D) $\frac{e^{-E/kT}}{2e^{-E/kT}+4e^{-2E/kT}}$

14. The thermodynamic relation expressing change of temperature with the volume at constant entropy $\left(\frac{\partial T}{\partial V}\right)_S$ is given by :

(A) $-T\left(\frac{\partial p}{\partial q}\right)_v$

(B) $T\left(\frac{\partial p}{\partial q}\right)_v$

(C) $-V\left(\frac{\partial p}{\partial q}\right)_T$

(D) $T\left(\frac{\partial p}{\partial q}\right)_T$

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15. If the free energy of a photon gas enclosed in a volume V is given by $G = -1/3\ aVT^4$, where a is a constant and T is the temperature of the gas. The chemical potential of this gas would be :
(A) 0 (B) $4/3\ aVT^3$
(C) $1/3\ aVT^4$ (D) aVT^4

16. According to Debye-Huckel theory, electrophorectic component of ionic velocity :
(A) Decreases with increase in ionic strength of solution
(B) Increases with increase in ionic strength of solution
(C) Does not depend on ionic strength of solution
(D) May increase or decrease with change in ionic strength as it depends upon the nature of ion

17. Ionic strengths of 0.15 molal KCl and 0.15 molal K_2SO_4 solutions are :
(A) 0.15 and 0.45 respectively
(B) 0.15 and 0.30 respectively
(C) 0.30 and 0.90 respectively
(D) 0.30 and 0.38 respectively

18. In case of adsorption with dissociation for an A_2 molecule :
(A) The fraction of surface that is bare at high concentration is directly proportional to the square root of concentration of A_2
(B) The fraction of surface that is bare at high concentration is inversely proportional to the square root of concentration of A_2
(C) The fraction of surface that is bare at high concentration is inversely proportional to the concentration of A_2
(D) The fraction of surface that is bare at high concentration is directly proportional to the concentration of A_2

19. Which of the following is INCORRECT statement ?
(A) Intensity of rotational spectral lines is determined primarily by Boltzamann distribution and degeneracy of rotational levels
(B) If the life time of an excited electronic state of a molecule is 10^{-8} s, then its natural line width in frequency would be 10^8 Hz
(C) In Raman spectroscopy, rotational transitions are carried out by intense, coherent, polarized and monochromatic beam of light in visible range
(D) The spacing between energy levels of an harmonic oscillator decreases with the increase in the vibrational quantum number

20. Which of the following is TRUE for systematic absences in X-ray diffraction for a monoatomic solid with face centered cubic structure ?
(A) The systematic absences occur for planes having h+k+l even
(B) The systematic absences do not occur for planes having all h, k, l either odd or even
(C) The systematic absences occur for planes having h, k, l odd but do not occur for planes having h, k, l even
(D) All the planes having any combination of h, k, l do not show the systematic absences

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21. When an electron in an excited atom X, falls from L to K shell, an X-ray is emitted. These X-rays were diffracted at an angle of 7.75° by the set of (200) planes of a cubic lattice with dimension 5.28 A°. The difference in the energy between K-shell and L-shell in X, assuming first order diffraction, is ($\sin 7.75° = 0.1349$) :

(A) 2.788×10^{-16} J

(B) 27.88×10^{-16} J

(C) 13.94×10^{-16} J

(D) 13.94×10^{-14} J

22. If the perturbation $H` = ax$, where a is a constant, is added to infinite square well potential $V(x) = 0$ for $0 \leq x \leq \pi$ and $V(x) = \infty$ otherwise. The first order correction to the ground state energy would be :

(A) $a\pi/2$ (B) $a\pi$

(C) $a\pi/4$ (D) $a\pi/\sqrt{2}$

23. The eigen functions of hydrogen atom contain which of the following ?

I. Legendre Polynomials

II. Laguerre Polynomials

III. Hermite Polynomials

(A) I, II and III (B) I and II

(C) I only (D) II only

24. Plot of *log(x/m)* vs *log(p)* showed a straight line inclined at an angle of 45°. If the pressure is 0.5 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be ($\log 5 = 0.699$) :

(A) 1 g (B) 2 g

(C) 3 g (D) 5 g

25. Which of the following compounds possess an enantiotopic atom ?

(A) Ethanol (B) Hexachlorobenzene

(C) Propane (D) Malonic acid

26. In the most stable chair conformer of trans-1, 4-dimethylcyclohexane :

(A) The two methyl groups are axial and are on the same side of the ring

(B) The two methyl groups are axial and are on the opposite sides of the plane of the ring

(C) C-1 methyl is equatorial and C-4 methyl is axial

(D) Both methyl groups are equatorial

27. Which of the following compounds is expected to have least pKa value ?

(A) Cyclopropene

(B) Cyclobutene

(C) Cyclopentadiene

(D) Cycloheptatriene

28. Which of the following amines is not expected to react with BF_3 ?

(A) Me_3N (B) $PhNH_2$

(C) $(Ph)_2NH$ (D) $(Ph)_3N$

29. Which among the following has least aromatic character ?

(A) Pyridine (B) Pyrrole

(C) Furan (D) Thiophene

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30. Which of the following compounds is strongest acid ?

(A) CH_3NO_2 (B) CH_3CN

(C) CH_3-CO-R (D) CH_3-CH=CH_2

31. The reactive intermediate generated during Hoffmann rearrangement is :

(A) A carbocation (B) A carbanion

(C) A carbine (D) A nitrene

32. For an effective cyclisation in a 4n+2 system, which of the following mode and motion lead to successful reaction ?

(A) Thermal/Conrotatory

(B) Thermal/Disrotatory

(C) Photochemical/Conrotatory

(D) Photochemical/Disrotatory

33. Which of the following pairs of 1,3-butadienes interact with each other to give 4-vinyl-cyclohexene under photolytic conditions ?

(A) $[Trans]_T$ and $[Cis]_T$

(B) $[Trans]_T$ and $[Cis]_{S0}$

(C) $[Trans]_{S0}$ and $[Cis]_T$

(D) $[Trans]_{S0}$ and $[Cis]_{S0}$

34. Robinson annulation involves :

(A) Intermolecular Micheal addition and intramolecular aldol condensation

(B) Intramolecular Micheal addition and intermolecular aldol condensation

(C) Intermolecular Micheal addition and intermolecular aldol condensation

(D) Intramolecular Micheal addition and intramolecular aldol condensation

35. Treatment of cyclohexane with hydroxylamine followed by acid catalysed rearrangement of the product yields :

(A) A lactone

(B) A ketoxime

(C) A six-membered lactone

(D) A seven-membered lactone

36. Formylation of 2-methylcyclohexanone in the presence of ethylformate and sodium ethoxide occurs :

(A) Exclusively at C-2

(B) Exclusively at C-6

(C) Both at C-2 and C-6

(D) More at C-6 and less at C-2

37. Which of the following combinations of synthons would give 1,3-difunctional compounds ?

(A) $a^1 + d^2$ (B) $a^2 + d^1$

(C) $a^2 + d^0$ (D) Both (A) and (B)

38. Woodward's modification of Prevost-hydroxylation is employed to bring about :

(A) Anti-hydroxylation of an alkene

(B) Syn-hydroxylation of an alkene from less hindered side

(C) Syn-hydroxylation of an alkene from the hindered side

(D) Anti-hydroxylation of an alkene though the initial attack of I_2 is from less hindered side

39. Which of the following is reduced by hydrogenation over palladium charcoal ?

(A) RCOCl (B) RCOOR'

(C) RCOOH (D) $RCONH_2$

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40. Assuming that the abundance of molecular ion peak of benzene is 100% in its mass spectrum, what would be the intensity of M+1 peak ?

(A) 1.1% (B) 11%

(C) 6.6% (D) 66%

41. The structure of a compound having molecular formula $C_9H_{10}O$ showing λ_{max} at 250 and 280 nm; ν_{max} at 1720 cm^{-1} and 3000 cm^{-1} and ^1H NMR signals at δ 7.3 (5H, m), 3.7 (2H, s) and 2.1 (3H, s) could be :

(A) $Ph-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

(B) $Ph-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(C) $H_3C-C_6H_4-\overset{O}{\overset{\|}{C}}-CH_3$

(D) $Ph-CH_2-CH_2-CHO$

42. Which of the following spectroscopic techniques is most easy and appropriate to differentiate between $H_3C-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$ and $H_2CH_3C-\overset{O}{\overset{\|}{C}}-OCH_3$

(A) UV-spectroscopy

(B) IR-spectroscopy

(C) ^1H-NMR-spectroscopy

(D) Mass spectroscopy

43. Which of the following units dimerise in tail to tail manner during biogenesis of triterpenoids ?

(A) 3,3-dimethyl allylpyrophosphate

(B) Geranyl pyrophosphate

(C) Farnesyl pyrophosphate

(D) Geranyl geranyl pyrophosphate

44. A flavonoid giving a phenylacetic acid and a phenol upon fusion with KOH and a deoxybenzoin upon refluxing with ethanolic KOH is :

(A) A flavones (B) An isoflavone

(C) An anthocyanin (D) A flavonol

45. Three moles of a compound A react with BH_3 to give a compound B which upon treatment with H_2O_2/OH yields 3 moles of 1-propanol. The compound B is:

(A) Propene

(B) Propylborane

(C) Triisopropylborane

(D) Tripropylborane

46. Addition of bromine across the olefinic bond in propane, in the presence of NaCl would yield :

(A) 1,2-dibromopropane and 1-bromo-2-chloropropane

(B) 1-chloro-2-bromopropane and 1,2-dibromopropane

(C) 1-bromo-2-chloropropane and 1-chloro-2-bromopropane

(D) 1,2-dibromopropane and 1,2-dichloropropane

47. Addition of HBr to (R)-3-chloro-1-butene would give :

(A) A pair of enantiomers

(B) A pair of diasterosisomers

(C) Two pairs of enantiomers

(D) Two pairs of diasterosisomers

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48. The path followed by the reaction of primary alkyl halide with ter-butoxide is :
(A) E2 (Minor) and S_N2 (Major)
(B) E2 (Major) and S_N2 (Minor)
(C) Only S_N2
(D) Only E2

49. Which of the following reagents would react with 1-bromobutane to yield exclusively E2 reaction product ?
(A) DBN or H^-
(B) Br^-/ HS^-
(C) RO^-/HO^-
(D) ROH/H_2O

50. Which of the following aryl halides would undergo fastest S_NAr reaction ?
(A) Ph-CN (B) Ph-COOEt
(C) Ph-NO_2 (D) Ph-$COCH_3$

51. Electronegativities of atoms _____ when crossing d block than while crossing the p block elements.
(A) Stay same
(B) Increase rapidly
(C) Decrease rapidly
(D) Change less rapidly

52. Choose the functionality that can be attached to Styrene and divinyl-benzene copolymer to make a strongly acidic cation exchanger ?
(A) Sulfonic acid groups
(B) Carboxylic acid groups
(C) Quaternary Ammonium groups
(D) Polyalkylamine groups

53. Which of the following class of σ bonded organo-transition metal compounds is much prone to beta elimination reaction ?
(A) Metal alkenyls
(B) Metal aryls
(C) Metal alkynyls
(D) Metal alkyls

54. What is incorrect for Sulfur Nitrogen compounds ?
(A) S_2N_2 has 6π and $S_3N_3^-$ has 10π e delocalization respectively
(B) S_4N_4 structure has a cradle conformation
(C) S_4N_2 has a six membered planar conformation
(D) Polythiazyl (SN)x has one unpaired electron on each S atom which leads to a one dimensional conductor/metal characteristics along the direction of (SN)x

55. Choose the missing fragment for the Isolobal series.
$Fe(CO)_4 \overset{o}{\longleftrightarrow} CR_2 \overset{o}{\longleftrightarrow}$
(A) $Re(CO)_4^-$ (B) CH_3
(C) $Mn(CO)_5$ (D) $Co(CO)_3$

56. $Fe(CO)_3$ fragment is capable of stabilizing which of the following reactive molecules ?
(A) Square planar cyclobutadiene
(B) Trimethylene methane
(C) 1-hydroxy-1,3-butadiene
(D) All of these

57. Which of the following compounds can be an efficient antidote for lead toxicity ?
(A) $CH_3CH(SH)CH_3$
(B) $CH_3CH(OH)CH_3$
(C) $CH_2(OH)CH(OH)CH_2(OH)$
(D) $CH_2(SH)CH(OH)CH_2(OH)$

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58. The reaction :

$(CH_3)_4 N^+Cl^- + FeCl_3 \xrightarrow{OPCl_3} (CH_3)_4N^+ FeCl_4^-$

represents a neutralization reaction in which acid base concept ?

(A) Lux Flood
(B) Usanovich
(C) Solvent System
(D) Lowry Bronsted

59. The $d\pi-\sigma^*$ type of Pi bonding is seen in the complex :

(A) $[W(CO)_3(PR_3)_2H_2]$
(B) $[Cr(Cl)_6]^{3-}$
(C) $[Cr(CN)_6]^{3-}$
(D) $[Ni(PPh_3)_4]^{2+}$

60. What is incorrect for cyclic phosphazenes ?

(A) All cyclic Phosphazenes are not Planar and absence/loss of planarity does not appear to make these any less stable
(B) Skeletal N atoms are weakly basic and can be protonated or can form Coordination complexes especially with electron releasing substituents on P atoms
(C) Phosphazene skeleton can be easily reduced electrochemically
(D) PNP unit has heteromorohic $p\pi-d\pi$ bonding between Np_z and $P(d_{xz})$ orbitals and homomorphic interactions of Np_z through $P(d_{yz})$ orbital

61. The spectroscopic methods capable of estimating back bonding in a transition metal carbonyl system include :

(A) ^{13}C NMR chemical shift
(B) C–O stretching frequency in IR spectroscopy
(C) M–C and C–O distances in X-ray diffraction measurement
(D) Any of these

62. The Kinetics of the ligand substitution reaction $Ni(CO_4 + L \longrightarrow Ni(CO)_3L + CO$ is expected to be :

(A) Overall second order; being first order in both complex and ligand L
(B) Overall zero order
(C) First order in complex and zero order in ligand L
(D) Zero order in complex and first order in ligand L

63. What is incorrect for Vitamin B_{12} ?

(A) It is nature's only organometallic compound which is fully explored structurally and mechanistically
(B) It is the only Vitamin known to contain a transition metal
(C) It is synthesized in all higher animals and is found in higher plants also
(D) Its mechanism of action is radical based and spans three cobalt oxidation states (Co^I, Co^{II} and Co^{III})

64. What is incorrect for Borazine ?

(A) Borazine is isoelectronic with benzene
(B) Borazine has similar physical and chemical properties as benzene
(C) Borazine and Benezene both have $p\pi$-$p\pi$ bonding
(D) Borazine has electron rich Nitrogen and electrophilic Boron atoms in ring structure

65. The shape of which of these molecules confer it a C_3V symmetry point group ?

(A) Trimethylborane
(B) Phosgene
(C) Ammonium tetrafluoroborate
(D) Phosphorous oxyfluoride

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66. What is incorrect for bonding in case of dinuclear metal clusters ?

(A) The nature of M-M bond can be different in different d^n systems

(B) The strength of M-M bond depends on the electronic structure of metal ions in the cluster

(C) $[Mo_2Cl_8]^{2-}$ has a staggered while $[Re_2Cl_8]^{2-}$ has eclipsed chloride ions

(D) None of these

67. Which of the following types of electronic transitions are observed in Actinides ?

(A) f – f transitions

(B) 5f → 6d transitions

(C) Charge transfer transitions

(D) All of these

68. Among the two olefin complexes :

(I) $[C_2H_4Pt(PPh_3)_2]$ and (II) $[C_2H_4Fe(CO)_4]$.

(A) (I) - has η^2 olefin structure

(B) Both (I) and (II) have η^2 olefin structure

(C) (I)- has metalacyclopropane structure

(D) Both (I) and (II) have metalacyclopropane structure

69. In case of outer sphere electron transfer mechanism of coordination compounds, the activation energy involves :

(A) Energy required to bring oxidant and reductant over a distance suitable for electron transfer

(B) Energy required for bond compression and stretching to achieve orbitals of equal energy

(C) Energy required for solvent reorganization outside coordination sphere

(D) All of these

70. Which of the following compounds will not undergo oxidative addition of methyl iodide ?

(A) $[Ir(PPh_3)_2(CO)Cl]$

(B) $[Rh\,I_2(CO)_2]^-$

(C) $[(\eta^5\,Cp)_2\,Ti(Me)Cl]$

(D) $[Ir(MeO)_2(CO)Cl]$

71. Which of the following pair of reagents will not react to form product ?

(A) $PF_5 + CsF$

(B) $XeF_6 + BF_3$

(C) $RbBr + BaBr_2$

(D) $NaF + AlF_3$

72. The migratory nature of insertion reaction was ascertained from decarbonylation of Cis $Mn^{13}CO(CH_3CO)(CO)_4$ using which product ratio analysis ?

(A) 25% untagged + 75% Cis ^{13}CO and methyl

(B) 25% untagged + 75% Trans ^{13}CO and methyl

(C) 25% untagged + 50% Cis and 25% Trans ^{13}CO and methyl

(D) 25% untagged + 50% Trans and 25% Cis ^{13}CO and methyl

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73. Correct sequence for the following borane types is :

$B_7H_7^{2-}$, B_6H_{10}, B_5H_{11}

(A) Closo, Nido, Arachno

(B) Nido, Closo, Arachno

(C) Arachno, Nido, Closo

(D) Closo, Arachno, Nido

74. The reaction of thiourea (Tu) with the geometrical isomers of $[Pt(NH_3)_2Cl_2]$ will produce :

(A) Tetra thiourea $[Pt(Tu)_4]^{2+}$ in case of cis isomer

(B) Bis thiourea $[Pt(Tu)_2(NH_3)_2]^{2+}$ in case of cis isomer

(C) Tetra thiourea $[Pt(Tu)_4]^{2+}$ in case of trans isomer

(D) $[Pt(Tu)_2(NH_3)_2]^{2+}$ in case of both cis and trans isomer

75. The number of metal–metal bonds in $(\mu\text{–}Br)_2[Mn(CO)_4]_2$:

(A) One (B) Two

(C) Three (D) Zero

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