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PHDURS-EE-2013

SUBJECT : Chemistry

B

10070

Sr. No. .....

Time : **1¼ Hours** Max. Marks : **100** Total Questions : **100**

Candidate's Name _____ Date of Birth _____

Father's Name _____ Mother's Name _____

Roll No. (in figures) _____ (in words) _____

Date of Examination _____ **Option Attempt (Under Part-II)** _____

_____ (Signature of the Candidate)

_____ (Signature of the Invigilator)

CANDIDATES MUST READ THE FOLLOWING INFORMATION/INSTRUCTIONS BEFORE STARTING THE QUESTION PAPER.

1. **Part-I** (Question No. 1 to 40) is compulsory. **Part-II** (Question Nos. 41 to 100) is Optional. From Part-II, the candidate is to attempt 60 questions from any **One Option** out of the **three Optional parts** i.e. either from Option "A" or "B" or "C". All questions carry equal marks.
2. All the candidates ***must return*** the question booklet as well as OMR Answer-Sheet to the Invigilator concerned before leaving the Examination Hall, failing which a case of use of unfair-means/misbehaviour will be registered against him/her, in addition to lodging of an FIR with the police. Further the answer-sheet of such a candidate will not be evaluated.
3. In case there is any discrepancy in any question(s) in the Question Booklet, the same may be brought to the notice of the Controller of Examinations in writing **within two hours** after the test is over. No such complaint(s) will be entertained thereafter.
4. The candidate ***must not*** do any rough work or writing in the OMR Answer-Sheet. Rough work, if any, may be done in the question booklet itself. Answers **Must Not** be ticked in the question booklet.
5. ***Only black or blue ball point pen is to be used in the OMR Answer-Sheet.***
6. For each correct answer, the candidate will get full credit. Cutting, erasing, overwriting and more than one answer in OMR Answer-Sheet will be treated as incorrect answer. There will be No Negative marking.
7. *Before answering the questions, the candidates should ensure that they have been supplied correct and complete booklet. Complaints, if any, regarding misprinting etc. will not be entertained* **30** *minutes after starting of the examination.*

PART – I
(COMPULSORY)

1. The wave length of de-Broglie's wave associated with a moving proton of mass 1.66×10^{-27} kg and kinetic energy of 5×10^{-27} J is :

   (1) 162.65×10^{-8} m (2) 16.265×10^{-8} m

   (3) 16.265 m (4) 1.6265 m

2. The pure rotational spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20.80 cm^{-1}. The value of rotational constant is :

   (1) 20.80 cm^{-1} (2) 10.40 cm^{-1} (3) 5.20 cm^{-1} (4) 2 cm^{-1}

3. Which of the following molecules has lowest vibrational stretching frequency ?

   (1) $^{1}H\ ^{35}Cl$ (2) $^{2}D\ ^{35}Cl$ (3) $^{1}H\ ^{36}Cl$ (4) $^{1}H\ ^{37}Cl$

4. The proton nmr spectrum of propane will consist of :

   (1) a triplet and a singlet (2) a triplet and a quartet

   (3) a doublet and a sixtet (4) a triplet and a septet

5. To check that a secondary alcohol has been completely oxidized to a ketone you can :

   (1) check out the IR spectrum has absorptions at 3500 cm^{-1} and 1650 cm^{-1}

   (2) check out the IR spectrum has no absorptions at 3500 cm^{-1} and 1650 cm^{-1}

   (3) check out the IR spectrum has no absorptions at 3500 cm^{-1}

   (4) check out the IR spectrum has no absorptions around 1650 cm^{-1}

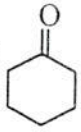
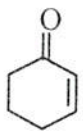
6. The β-isomer of hydrated trisglycinato cobalt (III) is ..... in colour consisting of two bands.

   (1) Red (2) Violet (3) Yellow (4) Blue

7. Which listed below gives only spin active nuclei ?

   (1) $^{1}H, ^{13}C, ^{19}F$ (2) $^{2}H, ^{12}C, ^{19}F$

   (3) $^{1}H, ^{2}H, ^{12}C$ (4) $^{1}H, ^{12}C, ^{19}F$

8. The position of the characteristic carbonyl stretching absorption bands in the IR spectrum of  and  are observed at :

(1) 1715 cm^{-1} and 1680 cm^{-1}
(2) 1680 cm^{-1} and 1715 cm^{-1}
(3) 1740 cm^{-1} and 1715 cm^{-1}
(4) 1715 cm^{-1} and 1740 cm^{-1}

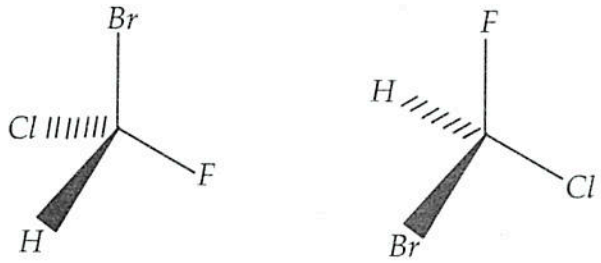
9. The lowest energy transition for tetrahedral complex of Mn^{2+} is :

(1) $^3A_2 \rightarrow T_1$ (2) $^4T_1 \rightarrow {}^4A_2$ (3) $^3A_2 \rightarrow {}^3T_2$ (4) $^4A_2 \rightarrow {}^4T_2$

10. The cis isomers often have ..... molar absorptivity values for d $\rightarrow$ d transitions than trans isomers.

(1) Larger (2) Smaller (3) Equal (4) None of the above

11. The two compounds shown below are :



(1) diasteromers
(2) enantiomers
(3) identical
(4) conformational isomers

12. Which of the following is ***not true*** about enantiomers ? They have the same :

(1) Melting Point
(2) Boiling Point
(3) Specific rotation
(4) Density

13. When benzyl chloride is treated with ethanolic KCN, benzyl ethyl, ether is produced along with benzyl cyanide. The most likely mechanism for the reaction would be :

(1) SN^2
(2) SN^1
(3) SN^i
(4) Both SN^1 and SN^2

14. The carbene which adds stereo specifically to a double bond is in the ..... state.
(1) singlet (2) doublet (3) triplet (4) free radical

15. The compound which would undergo nitration at ortho and para position with rates lower than that of benzene is :
(1) Cinnamic acid (2) Toluene (3) Phenol (4) Benzoic acid

16. M-effect is :
(1) Resonance effect (2) Inductive effect
(3) No bond resonance (4) Electromeric effect

17. The type of linkage present in porcion is :
(1) H-bonding (2) Covalent linkage
(3) Ionic bond (4) Coordinate bond

18. Epimers differ in :
(1) C – 1 (2) C – 2
(3) C – 1 and C – 2 (4) None of the above

19. In the conversion of a Grignard reagent into an aldehyde the other component used is :
(1) ethyl formate (2) ethyl acetate (3) ethyl cyanide (4) CO_2

20. Sulphonation of benzene differs from most other electrophilic substitution reaction in that the reaction :
(1) is reversible
(2) occurs with explosive violence
(3) requires elevated temperature
(4) requires Lewis acid catalyst

21. At 25°C which of the following substance has the lowest molar entropy ?
(1) N_2 (gas) (2) Mg(s) (3) $C_6H_6(l)$ (4) $CCl_4(g)$

22. The unit of the rate and rate constant are the same for a reaction of order :
(1) 0 (2) 1 (3) $\frac{1}{2}$ (4) 2

23. Walden role is given by :
(1) product of equivalent conductance and viscosity
(2) product of molarity and viscosity
(3) sum of viscosity and ionic conductance
(4) product of molarity and molecular mass

24. In Rice-Herzfeld mechanism of decomposition of acetaldehyde, the order of reaction is :
(1) 1/2 (2) 1 (3) 3/2 (4) 2

25. Clausius-Clapeyron equation is given by :
(1) $\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303\, R}\left[\frac{T_2 - T_1}{T_1 \times T_2}\right]$ (2) $\log \frac{p_1}{p_2} = \frac{\Delta H_{vap}}{2.303\, R}\left[\frac{T_1 - T_2}{T_1 \times T_2}\right]$
(3) $\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303}\left[\frac{T_1 - T_2}{T_1 + T_2}\right]$ (4) $\log \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303}\left[\frac{T_1 + T_2}{T_1 - T_2}\right]$

26. Which quantum number does not arise from solution of Schrodinger equation ?
(1) Principal quantum number (2) Spin quantum number
(3) Magnetic quantum number (4) Azimuthal quantum number

27. If length of the one dimensional box is halved, the energy of the partide will become :
(1) Half (2) Doubled
(3) Four times (4) One fourth

28. The degeneracy of energy level with energy equal to $\frac{6h^2}{8na^2}$ is :
(1) 2 (2) 3 (3) 6 (4) 9

29. Unit of equivalent conductivity is :
(1) ohm $cm^2 eq^{-1}$ (2) ohm^{-1} $cm^2 eq^{-1}$
(3) ohm $cm^{-2} eq^{-1}$ (4) ohm^{-1} $cm^{-2} eq^{-1}$

30. If K = equilibrium constant, Q = reaction quotient and G = Gibb's free energy, which of the following is true for a spontaneous reaction ?
(1) $\Delta G < \Delta G^\circ$ (2) $\Delta G > \Delta G^\circ$ (3) $K > Q$ (4) $K < Q$

31. The geometry of IF_8^- ion is :

(1) Pyramidal
(2) Tetrahedral
(3) Trigonal bipyramidal
(4) Square antiprismatic

32. Which of the following statement is ***false*** ?

(1) $[Cu(en)_2]^{2+}$ is more stable than $[Cu(NH_3)_4]^{2+}$

(2) $[FeF]^{2+}$ is stable than $[FeCl]^{2+}$

(3) $[Fe(CN)_6]^{4-}$ is less stable in comparison to $[Fe(CN)_6]^{3-}$

(4) $[Cu(NH_3)_4]^{2+}$ is less stable than $[Cd(NH_3)_4]^{2+}$

33. The coordination numbers of Ti(N) and O^{2-} in rutile are, respectively :

(1) 6 and 3 (2) 3 and 6 (3) 2 and 4 (4) 4 and 2

34. Recemization of a chiral complex such as $[Cr(ox)_3]^{3-}$ is least likely to occur by :

(1) a dissociative pathway

(2) a pathway involving a 5-coordinate species in which one ox^{2-} ligand is monodentate

(3) the Ray-Dutt twist mechanism

(4) the Bailer twist mechanism

35. In the base-catalysed substitution of Cl^- by OH^- in $[Co(NH_3)_5Cl]^{2+}$ under strongly basic conditions, the first step in the mechanism is :

(1) conversion of an ammine to amido ligand

(2) substitution of Cl^- by $[OH]^-$

(3) dissociation of Cl^- to give a 5-coordinate intermediate

(4) association of $[OH]^-$ to give a 7-coordinate intermediate

36. In tetrahedral complexes, which orbital is involved in σ as well as π bond according to MO theory :

(1) e (2) t_2 (3) a_1 (4) b

37. The term symbol for ground state of Ni is :

(1) $^7S_3$ (2) $^3F_4$ (3) $^3P_0$ (4) $^7F_2$

38. In which of the following configuration, the orbital contribution is quenched in octahedral field ?
(1) $t_2g^4eg^2$ (2) $t_2g^6eg^1$ (3) t_2g^4 (4) $t_2g^5eg^2$

39. Which of the following does ***not*** possess bridged CO ?
(1) $CO_2(CO)_8$ (2) $Fe_3(CO)_{12}$ (3) $Os_3(CO)_{12}$ (4) $Fe_2(CO)_9$

40. Which of the following will have highest CO stretching frequency ?
(1) $Cr(CO)_6$ (2) $Mn(CO)_6^+$ (3) $V(CO)_6^-$ (4) $Fe(CO)_4^{2-}$

PART – II
(OPTIONAL)
OPTION – A : INORGANIC CHEMISTRY

41. The detection limit for anodic stripping voltametry is :
(1) 10^{-2} to 10^{-4} m (2) 10^{-4} to 10^{-6} m
(3) 10^{-9} to 10^{-10} m (4) 10^{-5} to 10^{-7} m

42. Which of the following can be used as end point detection technique in Coulometric titrations ?
(1) Potentiometry (2) Amperometry
(3) Conductometry (4) Potentio, ampero and conductometry

43. A rotating Pt electrode is preferred over DME in the titration involving :
(1) Bromine (2) Ag^+ ion
(3) Fe^{2+} ion (4) Br, Ag^+ and Fe^{2+} all

44. In nuclear medicine imaging, radiopharmaceuticals are taken :
(1) Intravenously (2) Orally
(3) Both (1) and (2) (4) Neither (1) nor (2)

45. The mode of decay in radio Iodine-131 is :
(1) α-decay (2) β-decay (3) γ-decay (4) Neutron decay

46. The increased concentration of K^+ in extra cellular fluid causes :
(1) Hypokalemia (2) Hyperkalemia
(3) Addison's disease (4) Dysphea

47. Liver necrosis disease is caused by deficiency of :
(1) Calcium (2) Chromium (3) Selenium (4) Cobalt

48. Cancer causing chemicals are :
(1) Oxines & Azo compounds
(2) Urethanes & nitrosoamines
(3) Alkylating agents
(4) All of these

49. Which iron salt has minimum interference with tetracyclin drug absorption in gut ?
(1) Ferrous sulphate
(2) Ferrous fumerate
(3) Ferrous succinate
(4) Ferric – EDTA

50. Which of the following is a antiviral drug ?
(1) 1-methyl-2-mercaptoimidazole
(2) 1-methylisatin-3-thiosemicarbazone
(3) 2-formyl-pyridine thiosemicarbazone
(4) Aspirin

51. 1-methyl-2-mercaptoimidazole is used as potential agent for :
(1) Anti thyroid activity
(2) Anti cancer activity
(3) Anti bacterial activity
(4) Anti malarial activity

52. The concentration of Lithium in Plasma should be :
(1) 2.0 m mol/litre
(2) 0.4 – 1.6 m mol/litre
(3) 0.6 – 1.2 m mol/litre
(4) 2.0 – 2.4 m mol/litre

53. Chemical name of Vitamin B_{12} is :
(1) Cyanocobalamin
(2) Hydroxycobalamin
(3) Methylcobalamin
(4) Cyano-, hydroxy – and methyl cobalamin

54. Recommended Dietry allowances for a male (19-70 years) for Vitamin C is :
(1) 15 mg (2) 90 mg (3) 20 mg (4) 5.0 mg

55. Source for polyphenolic antioxidants are food such as :
(1) fresh fruits and vegetables
(2) whole wheat cereals and tea
(3) vegetable oils
(4) eggs

56. The heptacity of tropylium ion is :

(1) n^5 (2) n^1 (3) n^7 (4) n^3

57. Fluxional behaviour in a molecule can be detected by :

(1) IR spectroscopy (2) X-rays

(3) NMR spectroscopy (4) UV-Vis spectroscopy

58. Ziegler-Natta catalyst is :

(1) $TiCl_4 - AlEt_3$ (2) $RhCl(PPh_3)_3$ (3) $CO_2(CO)_8$ (4) $PdCl_4^{2-}$

59. Electrophilic Carbene ligands are also called :

(1) Fischer Carbene (2) Schrock Carbene

(3) Homonuclear Carbene (4) Heteronuclear Carbene

60. In Ferrocene, which metal orbital interacts with the composite ring orbitals C_pE_{1g} of ligand for the formation of covalent bonds :

(1) $4\,pz, 4\,px$ (2) $3\,dxz, 3\,dyz$

(3) $3\,dxy, 3d_{x^2-y^2}$ (4) $(DS)_x, (DS)_y$

61. The C = C infrared absorption peak of $\left[Mn(n^3 - C_3H_5)(CO)_4\right]$ appears at :

(1) 1620 cm^{-1} (2) 1570 cm^{-1} (3) 1505 cm^{-1} (4) 1520 cm^{-1}

62. Which metal alkyne complex is $4e^-$ donor ?

(1) $Pt^{II}Cl_2$ (p-toluidine) $Bu^+C \equiv C\,Bu^+$

(2) $Pt^0(PPh_3)_2(Ph\,C \equiv C\,Ph)$

(3) $[C_2H_2CO_2(CO)_6]$

(4) None of the above

63. Transition metal alkene complexes are readily attacked by :

(1) Electrophile

(2) Nucleophile

(3) Both Electrophile and Nucleophile

(4) No reaction with electrophile & nucleophile

64. Which of the following does ***not*** obey EAN rule ?

(1) $V(CO)_3(\pi - C_5H_5)(R_2C = C\,R_2)_2$ (2) $Co(CO)_2(\pi - C_5H_5)$

(3) $Fe(\sigma - C_5H_5)(\pi - C_5H_5)(CO)_3$ (4) $Cr(C_6H_6)(CO)_3$

65. Proton NMR spectrum of $(n^1Cp)(n^5Cp)Fe(CO)_2$ at ambient temperature shows :

(1) Two singlets of almost equal intensity

(2) A singlet and a multiplet of equal intensity

(3) One singlet of high intensity

(4) Two multiplets of equal intensity

66. The current due to supporting electrolyte is called :

(1) Residual Current (2) Diffusion Current

(3) Migration Current (4) Alternate Current

67. In anodic stripping voltametry, the concentration of metal ions is in the range of :

(1) 10^{-3} to 10^{-6} m (2) 10^{-4} to 10^{-7} m

(3) 10^{-5} to 10^{-8} m (4) 10^{-5} to 10^{-10} m

68. The half wave potential for Cu^{2+} in 1 M $NaOH$ is :

(1) – 1.12 V (2) – 0.41 V (3) – 1.53 V (4) – 1.46 V

69. The diffusion current in polarography is given by :

(1) $i_d = i_l - i_r$ (2) $i_d = i_l + i_r$ (3) $i_d = 2i_l - i_r$ (4) $i_d = i_l - 2i_r$

70. Ion-selective membrane used in ion selective electrodes are :

(1) Glass membranes (2) Crystalline membranes

(3) Ion exchange resin membranes (4) All of the above

71. The radioactivity detector based on light emission is :

(1) Cloud Chamber (2) Ionization Chamber

(3) Scintillation Counter (4) Solid State Detector

72. To which element, Neutron Activation Analysis is applicable ?

(1) Magnesium (2) Niobium (3) Vanadium (4) Copper

73. The sensitivity of NAA depends upon :

(1) Atomic cross section of particles (2) Flux of particles

(3) Half life of Nuclide (4) All of these

74. Ionization Chamber uses lower operating voltage than :

(1) Proportional Counters (2) Solid ion Chamber

(3) Scintillation Counter (4) All of these

75. Which of the following Nuclei is ***not*** doubly magic ?

(1) ${}^{4}_{2}He$ (2) ${}^{16}_{8}O$ (3) ${}^{208}_{82}Pb$ (4) ${}^{238}_{92}U$

76. The metal species present in Nitrogenase is :

(1) Zinc (2) Molybdenum (3) Tungsten (4) Lead

77. Which of the following is used in Psychotropic drugs ?

(1) Sodium fluoride (2) Lithium carbonate

(3) Barium sulphide (4) Zinc oxide

78. CYTOCHROM P-450 enzyme contains metal :

(1) Zinc (2) Copper (3) Cobalt (4) Iron

79. Deficiency of *Zn* causes the disease :

(1) Convulsions (2) Liver necrosis

(3) Dwarfism (4) Kinky-hair syndrome

80. Oxymyoglobin contains :

(1) Oxygen in hole of Porphyrin

(2) Oxygen bonded to *Mg*

(3) Oxygen at trans position to histidine chain

(4) Oxygen not present at all

81. Photochemical Smog is caused by :

(1) Oxides of Nitrogen (2) Hydrocarbons

(3) Carbon monoxide (4) Oxides of N, Hydrocarbons and *CO*

82. Ozone depletion in Antarctica is due to the formation of :
(1) Acrolin
(2) Peroxyacetylnitrate
(3) SO_2 and SO_3
(4) Chlorine nitrate

83. Silicoses is caused by :
(1) Acid rain
(2) Depletion of Ozone
(3) Inhalation of aerosols
(4) Inhalation of SO_2

84. Catechol type siderophore is :
(1) Ferrichrome
(2) Enterobactin
(3) Ferrioxamine
(4) None of these

85. In the resting state, the level of Ca^{2+} near the muscle fibre is :
(1) Very low
(2) Very high
(3) Medium
(4) No change

86. In CO_2 molecule, the band at 1340 cm^{-1} due to fermiresonance, has band maxima (doublet) at :
(1) 1286 and 1388 cm^{-1}
(2) 1276 and 1398 cm^{-1}
(3) 1277 and 1397 cm^{-1}
(4) None of these

87. In AB_5 type TBP molecules, the number of IR active stretching vibrations are :
(1) Three (2) Four (3) Two (4) Five

88. In thiocynato complexes, the $C \equiv N$ stretching frequencies are ..... than in isothiocynato complexes.
(1) Higher (2) Lower (3) Similar (4) None of these

89. Value of 'g' for an atom having ground state term symbol $^2P_{3/2}$ will be :
(1) 2.0 (2) 1.33 (3) 1.73 (4) 2.25

90. In EPR spectrum of bis (salicyladimine) copper (II), the hyperfine structure of each major peak consists of :
(1) Nine subpeaks
(2) Fifteen subpeaks
(3) Eleven subpeaks
(4) Ten subpeaks

91. Quadrupole splitting is ***not*** observed in the MB spectrum of :

(1) $Fe(CO)_5$ (2) $FeSO_4$ (3) $K_3[Fe(CN)_6]$ (4) $FeCl_3$

92. The radical anion $[ON(SO_3)_2]^{2-}$ shows in ESR :

(1) A triplet hyperfine structure from nitrogen

(2) Hyperfine splitting of 13.05 gauss

(3) No splitting due to S and O

(4) All of the above

93. Which is ***correct*** order of chemical shift (δ) decrease in MB spectra ?

(1) $Cl^- > O^{2-} > N^{3-} > CN^-$ (2) $CN^- > O^{2-} > N^{3-} > Cl^-$

(3) $Cl^- > CN^- > O^{2-} > N^{3-}$ (4) $CN^- > N^{3-} > O^{2-} > Cl^-$

94. Which does ***not*** apply to mass spectrometry ?

(1) Magnetic field (2) Acceleration potential

(3) Microwaves (4) Ionization and fragmentation

95. Which change is ***not*** detected by DTA ?

(1) Polymer softening (2) Desorption

(3) Sublimation (4) Loss of moisture

96. Stability of nucleus is due to :

(1) Long-range forces (2) Short-range forces

(3) Pion cloud only (4) None of the above

97. Which nuclear model can best explain that all elements with atomic number greater than 92 are radioactive ?

(1) Liquid Drop Model (2) Shell Model

(3) Collective Model (4) All of these

98. What is the total binding energy of ^6_3Li nucleus having atomic mass 6.0170 amu ?

(Mass of proton = 1.00727 a.m.u. and mass of neutron = 1.008665 amu)

(1) 28.82 MeV (2) 27.89 MeV (3) 28.69 MeV (4) 27.69 MeV

99. Spallation reactions are initiated by high speed :

(1) Protons (2) α-particles

(3) Both Protons and α-particles (4) None of these

100. $^{27}_{13}Al$ is a stable Isotope. It is expected to disintegrate by :

(1) α – emission (2) β^- emission (3) β^+ emission (4) Proton emission

OPTION – B : PHYSICAL CHEMISTRY

41. The step down ladder operator is :

(1) $\hat{J}_+ = \hat{J}_x + \hat{J}_y$ (2) $\hat{J}_+ = \hat{J}_x - \hat{J}_y$ (3) $\hat{J}_- = \hat{J}_x + i\hat{J}_y$ (4) $\hat{J}_- = \hat{J}_x - i\hat{J}_y$

where all the symbols have usual significance.

42. Molecules orbital theory :

(1) underestimates the importance of covalent structures

(2) overestimates the importance of ionic structures

(3) puts equal importance on both ionic and covalent structures

(4) None of the above

43. Operators $\hat{A}$ and $\hat{B}$ are said to be commutative, if :

(1) $\hat{A} + \hat{B} = 0$ (2) $\hat{A} - \hat{B} = 0$

(3) $\hat{A}\,\hat{B} + \hat{B}\,\hat{A} = 0$ (4) $\hat{A}\,\hat{B} - \hat{B}\,\hat{A} = 0$

44. Which of the following is ***correct*** ?

(1) $\left[\hat{L}^2, \hat{L}_z\right] > 0$ (2) $\left[\hat{L}^2, \hat{L}_z\right] < 0$

(3) $\left[\hat{L}^2, \hat{L}_z\right] = 0$ (4) $\left[\hat{L}^2, \hat{L}_z\right] = i\hbar\hat{L}_x$

45. Which of the following is ***true*** ?

(1) $q_{tr} >> q_{rot} >> q_{vib} >> q_{elect}$ (2) $q_{tr} >> q_{vib} > q_{rot} > q_{elect}$

(3) $q_{tr} << q_{rot} << q_{vib} << q_{elect}$ (4) $q_{tr} < q_{vib} < q_{rot} < q_{elect}$

where q_{tr}, q_{rot}, q_{vib} and q_{elect} are translational, rotational, vibrational and electronic partition function.

46. When *Pt* and *Co* are electrically connected, which one gets corroded ?

(1) *Pt* (2) *Co* (3) Cannot decide (4) None

47. Pipes of different materials, such as copper and steels, should not be embedded in a trench in close proximity to avoid :

(1) deposition of copper on steel pipe

(2) depassivation of steel

(3) corrosion of copper pipes

(4) galvanic corrosion

48. If moisture and dirt entrapment is a major problem, it would be good practice to :

(1) Spot weld (2) Skip weld (3) Stitch weld (4) Butt weld

49. The number of α and β particles emitted by ${}^{218}_{81}Ra$ in changing to a stable isotope of ${}^{206}_{82}Pb$ will be :

(1) 3 and 2 (2) 2 and 4 (3) 3 and 4 (4) 3 and 1

50. Milk is a/an :

(1) Emulsion (2) Gel (3) Suspension (4) Pure solution

51. At temperature near absolute zero, gaseous particles possess only :

(1) Translational energy (2) Vibrational energy

(3) Rotational energy (4) Rotational and vibrational energy

52. Lattice strength of various types of crystals vary as :

(1) Ionic > covalent > metallic > molecular

(2) Covalent > metallic > ionic > molecular

(3) Metallic > covalent > ionic > molecular

(4) Covalent > ionic > metallic > molecular

53. The energy per mole of light having wavelength of 85 nm is :

(1) 1.207×10^6 J mole^{-1} (2) 1.307×10^6 J mole^{-1}

(3) 1.407×10^6 J mole^{-1} (4) 1.507×10^6 J mole^{-1}

54. Which of the following has been used in the manufacture of non-inflammable photographic films ?

(1) Cellulose nitrate (2) Cellulose xanthate

(3) Cellulose perchlorate (4) Cellulose acetate

55. Which of the following is an irreversible cell ?

(1) $Zn / Zn^{2+} / AgCl / Ag$ (2) $Zn / H_2SO_4 / Ag$

(3) $Zn / Zn^{2+} // Cd^{2+} / Cd$ (4) $Cd / Cd^{2+} // KCl, Hg_2Cl_2(s) / Hg$

56. Marcus refined the RRK theory by taking into consideration :

(1) vibrations of the energized molecule

(2) rotations of the energized molecule

(3) all vibrations and rotation of the energized molecule

(4) None of these

which in turn led to RRKM theory

57. The steric factor, P is related to Entropy of activation, $\Delta S^{\#}$ by :

(1) $P = \frac{RT}{ZNh} \cdot e^{\Delta S^{\#}/R}$ (2) $P = \frac{RT}{ZNh} \cdot e^{-\Delta S^{\#}/R}$

(3) $P = \frac{RT}{h} \cdot e^{\Delta S^{\#}/R}$ (4) $P = \frac{R}{ZNh} \cdot e^{\Delta S^{\#}/RT}$

58. The Gibbs adsorption equation is :

(1) $\Gamma = \frac{-RT}{C} \cdot \frac{dc}{dr}$ (2) $\Gamma = \frac{-CT}{R} \cdot \frac{dr}{dc}$

(3) $\Gamma = \frac{-C}{RT} \cdot \frac{dr}{dc}$ (4) $\Gamma = \frac{-CT}{R} \cdot \frac{dc}{dr}$

where all the notations have usual significance.

59. The cell potential is a :

(1) Thermodynamic property (2) Colligative property

(3) Extensive property (4) Intensive property

60. How many normal modes of vibration are possible for benzene molecule ?

(1) 6 (2) 30 (3) 12 (4) 8

61. Synthetic fibres like nylon-66 are very strong because :

(1) They have linear molecules consisting of very long chains

(2) They have high molecular weights and high melting points

(3) They have a high degree of cross-linking by strong carbon-carbon bond

(4) They have linear molecules interlinked with forces like hydrogen bonding

62. Polyethene is :

(1) Thermosetting (2) Thermoplastic

(3) Both (1) and (2) (4) None of these

63. A solid acts as an adsorbent because it has :

(1) a definite shape (2) a high lattice energy

(3) unsaturated valencies (4) small pores in it

64. According to Langmuir adsorption isotherm, the amount of gas adsorbed at very high pressure :

(1) goes on decreasing with pressure

(2) goes on increasing with pressure

(3) increases first and decreases later with pressure

(4) reaches a constant limiting value

65. Lyophilic sols are more stable than lyophobic sols because :

(1) The colloidal particles are solvated

(2) The colloidal particles have positive charge

(3) The colloidal particles have no charge

(4) There are strong electrostatic repulsions between the negatively charged colloidal particles

66. Which statement corresponds to the case where the chemical shift difference between two coupling protons is less than five times the coupling constant ?

(1) An Ax pattern is observed

(2) An AB pattern is observed

(3) A first order spectrum is expected

(4) An undistorted binomial pattern is expected

67. Which of the following statement is false about NMR experiment ?

(1) The energy difference between two spin states depends on the strength of magnetic field

(2) When energy absorption occurs, the nuclei are said to be in resonance with the electromagnetic radiation

(3) The energy required to flip the spin of a proton is in the infrared region of the electromagnetic radiation

(4) None of these

68. The number of microstates for distributing three atoms among energy states, having three quanta of energy are :

(1) 1 (2) 6 (3) 10 (4) 3

69. The rotational energy possessed by atom having one degree of atom is :

(1) RT (2) kT (3) $\frac{1}{2}RT$ (4) $\frac{1}{2}kT$

70. Translational partition function, q_t is expressed by :

(1) $q_t = \frac{(2\pi mkT)^{3/2}V}{RT}$ (2) $\frac{(2\pi mkT)^{3/2}}{RT}$

(3) $q_t = \frac{(2\pi mRT)^{3/2}V}{RT}$ (4) $\frac{(2\pi mRT)^{3/2}}{T}$

71. Select the correction equation from the following :

(1) $\left(\frac{\partial V}{\partial T}\right)_S = \frac{C_v}{T}\left(\frac{\partial T}{\partial P}\right)_V$ (2) $\left(\frac{\partial S}{\partial V}\right)_T = \frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_P$

(3) $\left(\frac{\partial V}{\partial T}\right)_V = \frac{C_v}{T}\left(\frac{\partial T}{\partial P}\right)_V$ (4) $\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_P$

72. Which of the following is ***not*** a state function ?

(1) Work (2) Heat (3) Enthalpy (4) Entropy

73. The fundamental vibrational frequency of a molecule is 1035 cm^{-1}. Its force constant would be :

(1) $4\pi^2 c\mu^2(1035)\times 10^4$ (2) $4\pi^2 c^2\mu^2(1035)^2\times 10^2$

(3) $4\pi^2 c^2\mu(1035)^2\times 10^4$ (4) $4\pi^2 c^2\mu(1035)^2\times 10^2$

74. The pH of a solution is 6. Acid is added to decrease the pH to 4. The increase in hydrogen ion concentration is :

(1) Hundred times (2) Two times

(3) Thousand times (4) Ten times

75. The quantum yield of photochemical gas reaction $2\ HI \rightleftharpoons H_2 + I_2$ at wavelength 2400 Å is :

(1) 0.20 (2) 10^3 (3) 10 (4) 2

76. Which of the following statement is ***correct*** ?

(1) A triple point is invariant

(2) A triple point is monovariant

(3) A triple point is also called incongruent melting point

(4) Eutectic point is same as triple point

77. Mean free path of a gas molecule is :

(1) independent of pressure

(2) inversely proportional to temperature

(3) directly proportional to pressure

(4) None of these

78. Van't Hoff equation ; (at $c \rightarrow o$) for predicting molar mass of a polymer solution reduces to :

(1) $\lim_{c \to o}\left(\frac{\pi}{c}\right) = \frac{R}{M}$ (2) $\lim_{c \to o}\left(\frac{\pi}{c}\right) = \frac{T}{M}$

(3) $\lim_{c \to o}\left(\frac{\pi}{c}\right) = \frac{RT}{M}$ (4) $\lim_{c \to o}\left(\frac{\pi}{c}\right) = \frac{RM}{T}$

Where π is the osmotic pressure.

79. The heterogeneity of the polymer sample is called its :

(1) Polydispersity index (2) Monodispersity

(3) Average molecular mass (4) Polydispersity

80. Oriental polarizability α, is related to temperature T, as :

(1) $\alpha = \frac{\mu}{3kT}$ (2) $\alpha = \frac{\mu^2}{3kT}$ (3) $\alpha = \frac{\mu}{kT}$ (4) $\alpha = \mu\, kT$

where all the symbols have usual significance.

81. $\psi_{21(-1)}$ represents :

(1) 2 *s* orbital (2) $2p_x$ orbital (3) $2p_y$ orbital (4) $2p_z$ orbital

82. The average of a measurable property px, can be determined by employing relation :

(1) $< p_x >= \dfrac{\int \hat{p}_x \phi \phi^{@} d\tau}{\int \phi \phi^{@} d\tau}$ (2) $< p_x >= \dfrac{\int \phi\, \hat{p}_x \phi^{@} d\tau}{\int \phi \phi^{@} d\tau}$

(3) $< \hat{p}_x >= \dfrac{\int \phi \phi^{@} \hat{p}_x d\tau}{\int \phi \phi^{@} d\tau}$ (4) None of the above

83. $\left[x, \dfrac{d}{dx}\right]$ will yield :

(1) zero (2) 1 (3) –1 (4) 2

84. The Hamiltonian operator for a Helium atom is expressed by :

(1) $\hat{H} = \dfrac{-h^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \dfrac{e^2}{r_{12}}$

(2) $\hat{H} = \dfrac{-h^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \dfrac{ze^2}{r_1} + \dfrac{ze^2}{r_2}$

(3) $\hat{H} = \dfrac{-h^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \dfrac{ze^2}{r_1} - \dfrac{ze^2}{r_2} + \dfrac{e^2}{r_{12}}$

(4) $\hat{H} = \dfrac{-h^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \dfrac{e^2}{r_{12}} + \dfrac{ze^2}{r_1} + \dfrac{ze^2}{r_2}$

where ∇_1 and ∇_2 are Laplacien operators for electrons 1 and 2 respectively. All other symbols have usual significance.

85. The Eigen value is/can :

(1) always positive (2) always negative

(3) be zero (4) be positive as well as negative

86. The radius of $^{27}_{13}Al$ nucleous is :

(1) 4.5×10^{-15} m (2) 4.5×10^{-14} m

(3) 4.5×10^{-16} m (4) 4.5×10^{-13} m

87. Let a molecule AB_6 belongs to O_h point group. The point group that result if it is changed to AB_5C would be :

(1) D_{4h} (2) C_{2v} (3) C_{4v} (4) None of these

88. Water molecule belongs to point group :

(1) C_{3v} (2) C_{2v} (3) D_{4h} (4) D_{2h}

89. The hyperfine splitting constant, 'a' utilized to map the molecular orbital occupied by unpaired electron is related by :

(1) $a = Q^e$ (2) $A = Q/e$ (3) $a = Q + e$ (4) $A = Q - e$

where e is the unpaired density on a carbon atom.

90. The Mössbauer spectra of $K_4Fe(CN)_6$ and $[K_3Fe(CN)_5NO]$ consist of, respectively :

(1) one line each (2) two lines each

(3) two and four lines (4) one and two lines

91. The power output of a laser in which a 2.0 J pulse can be delivered in one nanosecond is :

(1) 2.0 GW (2) 0.20 GW (3) 20.0 GW (4) 0.02 GW

92. The Miller indices of crystal plane which cut through the crystal axis at $(2a, 3b, c)$ are :

(1) (236) (2) (326) (3) (623) (4) (362)

93. Frenkel defects appear in crystals, in which :

(1) positive ions are much larger than the negative ions

(2) positive ions are equal to negative ions in size

(3) negative ions are much larger than the positive ions

(4) None of the above

94. The coordination number of an atom in a face–centred cubic unit cell is :

(1) 1 (2) 6 (3) 8 (4) 12

95. The probability factor in collision theory of reaction rates should be interpreted in terms of :
(1) Enthalpy (2) Free energy (3) Entropy (4) Viscosity

96. NMR transition is shifted from the reference in a 400 MHz spectrometer by 529 Hz. The chemical shift is :
(1) 1.32 (2) 5.29 (3) 1.82 (4) 7.58

97. If activation energy of a certain reaction is zero, then rate constant will be equal to :
(1) infinity (2) A (3) zero (4) A^{-1}
where A is the frequency factor.

98. Which one of the following statements about ionization in mass spectrometer is *incorrect* ?
(1) Gaseous atoms are ionized by bombarding them with high energy electrons
(2) Atoms are ionized so they can be accelerated
(3) Atoms are ionized so they can be deflected
(4) It doesn't matter how much energy you use to ionize atoms

99. The region of an infra-red spectrum where many absorptions takes place is known as :
(1) Thumb print region (2) Hand print region
(3) Finger print region (4) Foot print region

100. No diffraction would result, if :
(1) $\lambda << 2d$ (2) $\lambda >> 2d$ (3) $\lambda \simeq 2d$ (4) $\lambda << d$

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41. Magic angle in degrees along z-direction in NMR is :
(1) 45.1 (2) 54.7 (3) 135.3 (4) 125.3

42. Boltzmann population excess for protons at 800 MHz at 298 K is :
(1) 16 (2) 32 (3) 48 (4) 128

43. ROH signal appears at about what ppm range in NMR ?
(1) 0.5 – 5.0 (2) 0.1 – 8.0 (3) 0.3 – 4.0 (4) 0.3 – 10.0

44. Which aromatic band shows fine structure in UV spectrum ?
(1) primary (2) secondary (3) tertiary (4) none

45. What is *incorrect* about electron impact ionization technique ?
(1) It always leads to the appearance of the parent peak in the mass spectrum
(2) It is a "hard" technique
(3) It involves more fragmentation of the parent peak in comparison to the Chemical Ionization (CI) technique
(4) It involves a potential of 50 – 70 eV for ionization

46. Which is *correct* pair about the use of a matrix in mass spectrometry ?
(1) ESI + MALDI (2) FAB + MALDI
(3) EI + MALDI (4) CI + MALDI

47. The NH protons in coproporphyrin absorb at about what ppm ?
(1) + 1.0 (2) (–) 2.0 (3) (+) 3.0 (4) (–) 4.0

48. The general chemical shift range for P-31 in ppm is :
(1) 0 - 500 (2) 0 - 600 (3) 0 - 700 (4) 0 – 1000

49. The number of orientations for B-11 with respect to applied field is :
(1) 2 (2) 3 (3) 4 (4) 5

50. Continuous wave NMR spectroscopy gives a spectrum which is :
(1) Frequency domain (2) Time domain
(3) Both of these (4) None of these

51. Which is a better Diels-Alder diene for reaction with maleic anhydride ?
(1) Furan (2) Pyrrole (3) Thiophene (4) Pyridine

52. The thermal ring opening reactions of cyclobutenes are :
(1) Conrotatory
(2) Disrotatory
(3) Conrotatory or disrotatory depending upon the reaction temperature
(4) Cannot be predicted

53. Which is ***not*** used in treatment of arthritis ?

(1) Glucosamine sulfate (2) Chondroitin sulfate

(3) Methylsulfonyl methane (4) Tosylchloride

54. Hexene-1 after reaction with metachloroperbenzoic acid followed by treatment with Lithium aluminium hydride and then with water in acidic medium gives :

(1) Hexane (2) Hexan-1-ol (3) Hexan-2-ol (4) None

55. Betaine is an intermediate in :

(1) Wittig Reaction (2) Stobbe Reaction

(3) Stephenson Reduction (4) MPV Reduction

56. What is ***incorrect*** for SN^1 reactions ?

(1) Rearrangement is possible

(2) Rate is affected by solvent polarity

(3) The strength of the nucleophile is important in determining the rate

(4) The order of reactivity is $3° > 2° > 1°$

57. Number of orientations with respect to applied magnetic field for deuterium is :

(1) 2 (2) 3 (3) 1 (4) 4

58. Aspartic acid shows :

(1) pKa_1 (2) pKa_2

(3) pKa_1 and pKa_2 (4) pKa_1, pKa_2 and pKa_3

59. Which is ***incorrect*** regarding grading of sugars ?

(1) Sucrose-1 (2) Fructose-1.75 (3) Lactose-6 (4) Saccharin-3500

60. In trimethylanilinium cation, the o, m and p-protons are deshielded because of :

(1) Resonance (2) Inductive effect

(3) Both of these (4) None of these

61. The protons of the middle carbon in allyl carbanion absorb at what ppm ?

(1) 2.46 (2) 4.75 (3) 1.5 (4) 6.28

62. Which of these enhances the absorption of Vitamin A ?
(1) Vit. E (2) Vit. K (3) DMG (4) None

63. The CH proton in isopropyl carbocation absorbs at what ppm ?
(1) 5.06 (2) 6.28 (3) 4.75 (4) 13.50

64. What is the ***correct*** decreasing order of reactivity towards electrophilic aromatic substitution ?
(1) Indole > Pyrrole > Pyridine (2) Pyrrole > Pyridine > Indole
(3) Pyrrole > Indole > Pyridine (4) Indole > Pyridine > Pyrrole

65. Which is an Anti-cancer drug ?
(1) Camptothecin (2) Captopril (3) Carprofen (4) Etodolac

66. Which is a formylanion equivalent ?
(1) 1, 4-dithiane (2) Ethyl chloroformate
(3) Nitromethane (4) Acetylene

67. The CH proton in allyl carbocation absorbs at what ppm ?
(1) 2.56 (2) 9.64 (3) 8.97 (4) 3.56

68. The carboxypeptidase enzyme contains :
(1) Zinc (II) and hydrolyzes COO bond
(2) *Mg* (II) and hydrolyzes COO bond
(3) Zinc (II) and hydrolyzes peptide bond
(4) *Mg* (II) and hydrolyzes peptide bond

69. What is ***correct*** about relaxation times ?
(1) $T_2 = T_1$ (2) $T_2 > T_1$ (3) $T_2 < T_1$ (4) None of these

70. CMR spectrum of camphor shows how many peaks for carbons ?
(1) 10 (2) 9 (3) 8 (4) 7

71. By which of these, acetophenone can be converted to phenol :
(1) m-CPBA followed by base catalyzed hydrolysis
(2) Conc. HNO_3
(3) Iodine and *NaOH*
(4) singlet oxygen followed by base catalyzed hydrolysis

72. Diazomethane with acetylene gives :

(1) Pyrazole (2) Pyrazoline (3) Piperidine (4) Pyrimidine

73. Which is used for treating Gout ?

(1) Reserpine (2) Atropine (3) Colchine (4) None

74. Cinnamoyl alcohol upon treatment with lead tetraacetate gives :

(1) Acetophenone (2) Cinnamic acid

(3) Propanal (4) Cinnamaldehyde

75. Which is a strong base ?

(1) Aniline (2) Cyclohexylamine

(3) Pyrrole (4) Quinoline

76. In SN^2 displacement on methyl bromide, which is most effective ?

(1) $C_2H_5O^{\Theta}$ (2) HO^{Θ} (3) $C_6H_5O^{\Theta}$ (4) CH_3COO^{Θ}

77. Of these which reacts fastest with N-bromosuccinimide (NBS) ?

(1) Toluene (2) Methane (3) Pyridine (4) Benzene

78. Generally, an increase in solvent polarity for the reaction between alkylhalide and OH^{Θ} :

(1) Increases the rate of SN^1 reaction

(2) Decreases the rate of SN^2 reaction

(3) Increases the rate of SN^2 reaction

(4) Does not change the rate of SN^1 and SN^2 reactions

79. Which of these is the best leaving group ?

(1) Chloride (2) Fluoride (3) Tosylate (4) None

80. Of these which is least reactive ?

(1) CH_2N_2 (2) $CH_2=C=O$ (3) $:CH_2$ (4) $\cdot\dot{C}H_2$

81. By adding sodium dodecyl sulfate during the electrophoresis of proteins, it is possible to :

(1) determine a proteins isoelectric point

(2) determine an enzymes specific activity

(3) preserve a proteins native structure

(4) determine the amino acid composition

82. The triplet carbene with cis-alkene gives :

(1) cis-product (2) trans-product

(3) both cis and trans products (4) no product

83. DNFB is used to identify the N-terminal amino acid of peptides. What is this reagent called ?

(1) Van-Slyke Reagent (2) Sorenson Reagent

(3) Sanger's Reagent (4) None of these

84. Internal reference for F-19 is :

(1) NaF (2) CF_4 (3) $CFCl_3$ (4) NH_4F

85. What is the internal reference for N- 15 ?

(1) Liq. NH_3 (2) NH_4OH (3) NH_4Cl (4) NH_4F

86. Which is ***not*** an anticancer drug ?

(1) Vincristine (2) Cyclophosphamide

(3) Doxorubicin (4) Gabapentin

87. What kind of spectroscopy is FT NMR ?

(1) Absorption (2) Emission (3) Both of these (4) None

88. The presence of a bromine is indicated in a compound if its mass spectrum shows M and M + 2 peaks in the intensity ratio :

(1) 2 : 1 (2) 3 : 1 (3) 1 : 1 (4) 1 : 2

89. LAH in combination with $AlCl_3$ can be used to convert diarylketone (Ar_2CO) into :

(1) Ar_2CHOH (2) Ar_2CH_2 (3) $ArCHOAr$ (4) $Ar - Ar$

90. 1, 3-Dithiane is a structural equivalent of :

(1) Acylcarbanion (2) Formylcarbanion

(3) Acyl carbonium ion (4) Formylcarbonium ion

91. Select the right decreasing order of nucleophilicity :

(1) $CH_3-\overset{\Theta}{C}H_2 > \overset{\Theta}{N}H_2 > CH\equiv\overset{\Theta}{C} > \overset{\Theta}{O}H$

(2) $CH\equiv\overset{\Theta}{C} > \overset{\Theta}{N}H_2 > CH\equiv\overset{\Theta}{C} > \overset{\Theta}{O}H$

(3) $\overset{\Theta}{O}H > \overset{\Theta}{N}H_2 > CH\equiv\overset{\Theta}{C} > CH_3-\overset{\Theta}{C}H_2$

(4) $\overset{\Theta}{N}H_2 > CH\equiv\overset{\Theta}{C} > \overset{\Theta}{O}H > CH_3\overset{\Theta}{C}H_2$

92. The ratio M | M + 2 for the presence of chlorine in a compound in its mass spectrum is :

(1) 3 : 1 (2) 1 : 2 (3) 4 : 2 (4) 2 : 1

93. Which is right about stretching frequencies of C = C and C = O in i. r. spectroscopy from intensity point of view ?

(1) $V_{C=O}$ is stronger than $V_{C=C}$

(2) $V_{C=O}$ is weaker than $V_{C=C}$

(3) $V_{C=O}$ and $V_{C=C}$ have equal intensity

(4) None of these

94. What is the decreasing order of chemical shifts for protons among these compounds ?

(1) Alkynes > Alkanes > Alkenes (2) Alkynes > Alkenes > Alkanes

(3) Alkanes > Alkynes > Alkenes (4) Alkenes > Alkynes > Alkanes

95. Mass spectroscopy requires a minimum sample size of :

(1) Micrograms (2) Nanograms (3) Picograms (4) Grams

96. Internal reference for phosphorus-31 is :

(1) H_3PO_2 (85%) (2) H_3PO_4 (85%) (3) H_3PO_3 (85%) (4) None of these

97. Oct-4-ene shows C = C frequency in its i. r. spectrum at :

(1) 1680 – 1600 cm^{-1} (vw) (2) 1680 – 1600 cm^{-1} (s)

(3) 1680 – 1600 cm^{-1} (m) (4) No peak in this region

98. Continuous wave NMR spectroscopy involves :

(1) simultaneous detection of all resonances

(2) sequential detection of resonances of nuclei

(3) first simultaneous followed by sequential detection of resonances

(4) sometimes sequential and sometimes simultaneous detection of resonances

99. The C_{60} fullerene shows lesser number of peaks in the i. r. spectrum because :

(1) It contains a graphite like structure

(2) It is asymmetric

(3) It contains sp^3, sp^2 and sp carbons

(4) It has a symmetrical structure

100. Carbonyl compounds exhibit the transition :

(1) $\sigma - \sigma^* 2\,\pi - \pi^*$

(2) $\sigma - \pi^*,\ \pi - \pi^*,\ n - \pi^*$

(3) $\sigma - \sigma^*,\ n - \sigma^*,\ \pi - \pi^*$

(4) None of these