21. Which of the following pairs has the highest difference in their first ionization energy?
(a) Xe, Cs  
(b) Kr, Rb  
(c) Ar, K  
(d) Ne, Na

22. The ligand in uranocene is:
(a) $\text{C}_8\text{H}_8^-$  
(b) $\text{C}_5\text{H}_2^-$  
(c) $\text{C}_6\text{H}_6$  
(d) $\text{C}_4\text{H}_2^-$

23. In metal-olefin interaction, the extent of increase in metal $\rightarrow$ olefin $\pi$-back donation would
(a) lead to a decrease in C = C bond length
(b) change the formal oxidation state of the metal
(c) change the hybridisation of the olefin carbon from $\text{sp}^2$ to $\text{sp}^3$
(d) increase with the presence of electron donating substituent on the olefin.

24. The oxidation state of molybdenum in $\text{[}\eta^7$-tropylium$\text{]}\text{Mo(CO)}_3\text{]}^+$ is:
(a) +2  
(b) +1  
(c) 0  
(d) –1

25. The reaction of $\text{[PtCl}_2\text{]}^{2-}$ with two equivalents of $\text{NH}_3$ produces
(a) cis − $\text{[Pt(NH}_3\text{)}_2\text{Cl}_2\text{]}$  
(b) trans − $\text{[Pt(NH}_3\text{)}_2\text{Cl}_2\text{]}$  
(c) boths cis − $\text{[Pt(NH}_3\text{)}_2\text{Cl}_2\text{]}$ and trans − $\text{[Pt(NH}_3\text{)}_2\text{Cl}_2\text{]}$  
(d) cis − $\text{[Pt(NH}_3\text{)}_2\text{Cl}_4\text{]}^{2-}$

26. The electronic transition responsible for the color of the transition metal ions is
(a) $d_n \rightarrow d_n$  
(b) $d_n \rightarrow d_n$  
(c) $d_n \rightarrow d_n$  
(d) $d_n \rightarrow d_n$.

27. The number of metal-metal bonds in $\text{[W}_2\text{(OPh)}_6\text{]}$ is:
(a) 1  
(b) 2  
(c) 3  
(d) 4

28. The Mulliken symbols for the spectroscopic states arising from the free-ion term $\text{F}$ are
(a) $T_{2g} + E_g$  
(b) $T_{1g} + T_{2g} + T_{1u}$  
(c) $T_{1g} + T_{2g} + A_{2g}$  
(d) $A_{1g} + T_{2g} + T_{1g}$

29. Which of the following is used as propellant for whipping creams?
(a) $\text{N}_2\text{O}$  
(b) $\text{NO}$  
(c) $\text{N}_2\text{O}_3$  
(d) $\text{N}_2\text{O}_5$

30. Flame proof fabrices contain
(a) $\text{H}_2\text{NC(O)}\text{NH}_2\text{Na}_2\text{SO}_4$  
(b) $\text{H}_2\text{NC(S)}\text{NH}_2\text{Na}_2\text{SO}_4$

(c) $\text{H}_2\text{NC(O)}\text{NH}_2\text{H}_3\text{PO}_4$  
(d) $\text{H}_2\text{NC(S)}\text{NH}_2\text{H}_3\text{PO}_4$

31. Among the compounds A-D, those which hydrolyse easily are
(a) $\text{NCl}_3$  
(b) $\text{NF}_3$  
(c) $\text{BiCl}_3$  
(d) $\text{PCl}_3$.

32. The coordination geometry of copper (II) in the type I copper protein plastocyanin is:
(a) square planar  
(b) tetrahedral  
(c) octahedral  
(d) distorted tetrahedral

33. The metal ions present in the active site of nitrogenase enzyme co-factor are
(a) Fe, Mo  
(b) Fe, W  
(c) Fe, Cu  
(d) Fe, Ni
34. The reaction, \( [(CO)_5 \text{Mn(Me)}] + \text{CO} \rightarrow [(CO)_5 \text{Mn(CO)}\text{Me}] \) is an example for
   (a) oxidative addition \hspace{1cm} \text{(b) electrophilic substitution}
   (c) nucleophilic substitution \hspace{1cm} \text{(d) migratory insertion}

35. The number of EPR signals observed for octahedral Ni(II) complexes is
   (a) One \hspace{1cm} \text{(b) Two} \hspace{1cm} \text{(c) Three} \hspace{1cm} \text{(d) Zero}

36. For neutron activation analysis of an element, the favourable characteristics of both the target and the product are from the following
   (A) high neutron cross-section area of target
   (B) long half-life of the product
   (C) low neutron cross-section area of target
   (D) low half-life time of the product.
   The correct characteristics from the above are
   (a) A and B \hspace{1cm} \text{(b) C and D} \hspace{1cm} \text{(c) B and C} \hspace{1cm} \text{(d) A and D}

37. The concentrations of a species A undergoing the reaction \( A \rightarrow P \) is \( 1.0, 0.5, 0.33, 0.25 \) mol dm\(^{-3}\) at \( t = 0, 1, 2 \) and 3 seconds, respectively. The order of the reaction is:
   (a) two \hspace{1cm} \text{(b) one} \hspace{1cm} \text{(c) zero} \hspace{1cm} \text{(d) three}

38. The difference in energy levels of \( n = 2 \) and \( n = 1 \) of a particle -in- a one dimensional box is 6 units of energy. In the same units, what is the difference in energy levels of \( n = 3 \) and \( n = 2 \) for the above system?
   (a) 4 \hspace{1cm} \text{(b) 5} \hspace{1cm} \text{(c) 9} \hspace{1cm} \text{(d) 10}

39. The wave function \( \psi \) of a certain system is the linear combination
   \[ \psi = \sqrt{\frac{1}{4}} \psi_1 + \sqrt{\frac{3}{4}} \psi_2 \]

   where \( \psi_1 \) and \( \psi_2 \) are energy eigen functions with eigen values (non-degenerate) \( E_1 \) and \( E_2 \), respectively. What is the probability that the system energy will be observed to be \( E_1 \)?
   (a) \( \frac{3}{16} \) \hspace{1cm} \text{(b) \( \frac{3}{4} \)} \hspace{1cm} \text{(c) \( \frac{1}{4} \)} \hspace{1cm} \text{(d) \( \frac{1}{4} \)}

40. What is the atomic term symbol for helium atom with electronic configuration \( 1s^2 \)?
   (a) \( ^2S^\frac{1}{2} \) \hspace{1cm} \text{(b) \( ^1P^0 \)} \hspace{1cm} \text{(c) \( ^1S^0 \)} \hspace{1cm} \text{(d) \( ^1S^1 \)}

41. A molecule contains the following symmetry operations: \( E, 2C_6, 2C_3, C_2, 3\sigma_d, 3\sigma_v \). The number of classes and order of the symmetry point group is:
   (a) 3, 12 \hspace{1cm} \text{(b) 5, 12} \hspace{1cm} \text{(c) 6, 12} \hspace{1cm} \text{(d) 6, 6}

42. A triatomic molecule of the type \( AB_2 \) shows two IR absorption lines and one IR-Raman line. The structure of the molecule is:
   (a) \( B - B - A \) \hspace{1cm} \text{(b) \( B - A - B \)} \hspace{1cm} \text{(c) \( B - A - B \)} \hspace{1cm} \text{(d) \( A - B \)}

43. In NMR spectroscopy, the product of the nuclear ‘\( g \)’ factor (\( g_N \)), the nuclear magneton (\( \beta_N \)) and the magnetic field strength (\( B_0 \)) gives the
   (a) energy of transition from \( \alpha \) to \( \beta \) state \hspace{1cm} \text{(b) chemical shift}
   (c) spin-spin coupling constant \hspace{1cm} \text{(d) magnetogyric ratio}
44. An aqueous mixed solution of NaCl and HCl is exactly neutralized by an aqueous NaOH solution. The number of components in the final mixture is
(a) 1  (b) 2  (c) 3  (d) 4

45. The lowest pressure at which the liquid phase of a pure substance can exist is known as
(a) critical point pressure  (b) super-incumbent pressure
(c) triple-point pressure  (d) saturation vapour pressure.

46. A chemical reaction involving nonlinear molecule + nonlinear molecule $\implies$ nonlinear activated complex
The number of vibrational degrees of freedom in the activated complex, containing N atoms, is
(a) 3N–5  (b) 3N–6  (c) 3N–7  (d) 3N–8

47. Calculate the total number of microstates for 6 identical particles with their occupation numbers {1, 2, 3} in three states is:
(a) 6  (b) 12  (c) 60  (d) 720

48. If the concentration (c) is increased to 4 times its original value (c), the change in molar conductivity for strong electrolytes is (where b is Kohlrausch constant)
(a) 0  (b) $b\sqrt{c}$  (c) $2b\sqrt{c}$  (d) $4b\sqrt{c}$

49. In atom recombination reactions
(a) $E_a = 0, \Delta S^\circ = +ve, \Delta H^\circ = +ve$  (b) $E_a = 0, \Delta S^\circ = -ve, \Delta H^\circ = -ve$
(c) $E_a = +ve, \Delta S^\circ = -ve, \Delta H^\circ = -ve$  (d) $E_a = +ve, \Delta S^\circ = +ve, \Delta H^\circ = +ve$

50. In the Lindemann mechanism of unimolecular reactions, the observed order at low concentration is
(a) 0.5  (b) 1  (c) 1.5  (d) 2

51. The aggregation of surfactant molecules is known as
(a) micelles  (b) clusters  (c) gel  (d) colloid

52. The coordinates for the atoms in a body centred cubic unit cell are
(a) (0, 0, 0) and (1/2, 0, 0)  (b) (0, 0, 0) and (1/2, 1/2, 1/2)
(c) (0, 0, 0) and (0, 1/2, 0)  (d) (0, 0, 0) and (0, 0, 1/2)

53. The inter planar distance (Å) for a (100) plane in a cubic structure with the lattice parameter of 4Å is:
(a) 1  (b) 2  (c) 4  (d) 8

54. The correlation coefficient of two parameters is found to be -0.99. It may be concluded that the two parameters are
(a) strongly correlated  (b) almost uncorrelated
(c) connected by a cause-effect relationship  (d) not connected by a cause-effect relationship

55. The IUPAC name for the compound given below is

(a) (2R, 3Z)-7-phenylhept-3-en-2-ol  (b) (2S, 3Z)-7-phenylhept-3-en-2-ol
(c) (2R, 3E)-7-phenylhept-3-en-2-ol  (d) (2S, 3E)-7-phenylhept-3-en-2-ol

56. Among the following esters, the one that undergoes acid hydrolysis fastest is
(a)  (b)  (c)  (d)

57. Reaction of cyclohexyl benzyl ether with hydrogen in the presence of 10% Pd/C yields
(a) cyclohexanol and toluene  (b) cyclohexanol and benzyl alcohol
(c) cyclohexane and benzyl alcohol  (d) cyclohexane and toluene
58. Among the following dibromocyclohexanes, the one that reacts fastest with sodium iodide to give cyclohexene is

(a) ![Dibromocyclohexane A](image)
(b) ![Dibromocyclohexane B](image)
(c) ![Dibromocyclohexane C](image)
(d) ![Dibromocyclohexane D](image)

59. Match the following drugs with their medicinal activity
(A) 5-fluorouracil (i) anti-bacterial
(B) amoxicillin lowering (ii) cholesterol
(iii) anticancer
(iv) anti-inflammatory

(a) A-i, B-ii (b) A-iv, B-iii (c) A-iii, B-iv (d) A-iii, B-i

60. The major product formed in the following reaction sequence is

1. CH₃CO₂H
2. LiAlH₄

(a) ![Product A](image)
(b) ![Product B](image)
(c) ![Product C](image)
(d) ![Product D](image)

61. The biosynthetic precursor for the steroids is
(a) secologanin (b) shikimic acid (c) mevalonic acid (d) α-ketoglutaric acid

62. The major product formed in the following reaction sequence is

1. ⁷Bu₃SnCl, NaBH₄, AlBN
2. H₂SO₄, CrO₃

(a) ![Product A](image)
(b) ![Product B](image)
(c) ![Product C](image)
(d) ![Product D](image)

63. In the compound given below, the hydrogens marked A and B are

(a) homotopic (b) isotopic (c) enantiotopic (d) diastereotopic
64. In the IR spectrum, the absorption band due to carbonyl group in phenyl acetate appears at
   (a) 1800 cm\(^{-1}\)  (b) 1760 cm\(^{-1}\)  (c) 1710 cm\(^{-1}\)  (d) 1660 cm\(^{-1}\)

65. The reactive intermediate involved in the following reaction is:

   \[
   \begin{align*}
   \text{Br} & \quad \text{NaNH}_2 \\
   & \quad \text{Me} \\
   \text{NH} & \quad \text{N} \\
   \text{Me} & \\
   \end{align*}
   \]
   (a) a carbocation    (b) a carbanion    (c) a free radical    (d) an aryne

66. Number of isoprene units present in lupeol is

   \[
   \begin{align*}
   &\quad \text{HO} \\
   &\quad \text{CH}_3 \\
   &\quad \text{CH}_3 \\
   &\quad \text{CH}_3 \\
   &\quad \text{CH}_3 \\
   &\quad \text{HO} \\
   \end{align*}
   \]
   (a) two    (b) four    (c) six    (d) eight

67. The heterocyclic ring present in the amino acid histidine is:
   (a) pyridine    (b) tetrahydropyrrole    (c) indole    (d) imidazole

68. The gauche conformation \((\varphi = 60^\circ)\) of n-butane possesses
   (a) plane of symmetry; and is achiral    (b) \(C_\text{2}\)-axis of symmetry; and is chiral
   (c) centre of symmetry; and is achiral    (d) plane of symmetry; and is chiral

69. The following photochemical conversion proceeds through

   \[
   \begin{align*}
   &\quad \text{Me} \\
   &\quad \text{Me} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{Me} \\
   &\quad \text{Me} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{Me} \\
   &\quad \text{Me} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{Me} \\
   &\quad \text{Me} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{Me} \\
   &\quad \text{Me} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{Me} \\
   &\quad \text{Me} \\
   \end{align*}
   \]
   (a) Barton reaction    (b) Paterno-Büchi reaction
   (c) Norrish type I reaction    (d) Norrish type II reaction

70. Among the following dienes, the one that undergoes a degenerate Cope rearrangement is

   \[
   \begin{align*}
   &\quad \text{H} \\
   &\quad \text{H} \\
   &\quad \text{H} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{H} \\
   &\quad \text{H} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{H} \\
   &\quad \text{H} \\
   \end{align*}
   \]
   \[
   \begin{align*}
   &\quad \text{H} \\
   &\quad \text{H} \\
   \end{align*}
   \]
   (a)    (b)    (c)    (d)
PART-C

71. A radioisotope $^{41}$Ar initially decays at the rate of 34,500 disintegrations/minute, but decay rate falls to 21,500 disintegrations/minute after 75 minutes. The $t_{1/2}$ for $^{41}$Ar is:
(a) 90 minutes  
(b) 110 minutes  
(c) 180 minutes  
(d) 220 minutes.

72. The orders of reactivity of ligands, NMe$_3$, PMe$_3$ and CO with complexes MeTiCl$_3$ and (CO)$_5$Mo(thf) are
(a) CO > PMe$_3$ > NMe$_3$ and CO > NMe$_3$ > PMe$_3$
(b) PMe$_3$ > CO > NMe$_3$ and PMe$_3$ > CO > PMe$_3$
(c) NMe$_3$ > PMe$_3$ > CO and CO > PMe$_3$ > NMe$_3$
(d) NMe$_3$ > CO > PMe$_3$ and PMe$_3$ > NMe$_3$ > CO.

73. The number of lone-pairs are identical in the pairs
(a) XeF$_4$, ClF$_3$
(b) XeO$_4$, ICl$_4$–
(c) XeO$_2$F$_2$, ICl$_4$–
(d) XeO$_4$, ClF$_3$.

74. Among the following, those can act as Mössbauer nuclei are
(A) $^{129}$I,  
(B) $^{57}$Co  
(C) $^{57}$Fe  
(D) $^{121}$Sb
(a) A, B, C and D  
(b) B, C and D only  
(c) A, B, and D only  
(d) A, C and D only.

75. Which of the pairs will generally result in tetrahedral coordination complexes, when ligands are Cl$^-$ or OH$^-$
(A) Be(II), Ba(II)  
(B) Ba(II), Co(II)  
(C) Co(II), Zn(II)  
(D) Be(II), Zn(II)
(a) A and B  
(b) B and C  
(c) C and D  
(d) A and D.

76. Silica gel contains [CoCl$_4$]$^{2–}$ as an indicator. When activated, silica gel becomes dark blue while upon absorption of moisture, its colour changes to pale pink. This is because,
(a) Co(II) changes its coordination from tetrahedral to octahedral.
(b) Co(II) changes its oxidation state to Co(III)
(c) Tetrahedral crystal field splitting is NOT equal to octahedral crystal field splitting.
(d) Co(II) forms kinetically labile while Co(III) forms kinetically inert complexes.

77. For the metalloprotein hemerythrin, the statement that is NOT TRUE is
(a) there are two ion centres per active site.
(b) both iron centres are hexacoordinated in the active state.
(c) one iron is hexacoordinated while the other is pentacoordinated in the active state.
(d) it is found in marine invertebrates.

78. For a tetragonally distorted Cr(III) complex, zero-field splitting results in the following number of Kramers doublets:
(a) 1  
(b) 2  
(c) 3  
(d) 4.

79. Intense band at 15000 cm$^{-1}$ in the UV-visible spectrum of [Bu$_4$N]$_2$Re$_2$Cl$_8$ is due to the transition
(a) $\pi^–\pi^+$  
(b) $\delta^–\delta^*$  
(c) $\delta^–\pi^+$  
(d) $\pi^–\delta^*$.

80. Electron change in reduction of Ce(SO$_4$)$_2$, KMnO$_4$, HNO$_2$ and I$_2$ with hydrazine in acidic medium, respectively is
(a) 1e, 1e, 2e and 4e  
(b) 1e, 3e, 2e and 4e  
(c) 2e, 3e, 1e and 4e  
(d) 2e, 4e, 1e and 3e.

81. The compound that will behave as an acid in H$_2$SO$_4$ is
(a) CH$_3$COOH  
(b) HNO$_3$  
(c) HClO$_3$  
(d) H$_2$O.

82. Among the oxides of nitrogen, N$_2$O$_3$, N$_2$O$_4$ and N$_2$O$_5$, the compound(s) having N–N bond is/are
(a) N$_2$O$_4$ and N$_2$O$_5$
(b) N$_2$O$_4$ and N$_2$O$_3$
(c) N$_2$O$_3$ and N$_2$O$_4$
(d) N$_2$O$_5$ only.

83. The treatment of PhBr with n-BuLi yields:
(a) 2 n-BuPh + Br$_2$ + Li$_2$  
(b) PhPh + octane + 2 LiBr  
(c) n-BuPh + LiBr  
(d) PhLi + n-BuBr.
84. Though cyclobutadiene \((C_4H_4)\) is highly unstable and readily polymerizes in its free state, its transition metal complexes could be isolated because
(a) it engages in long-range interaction with transition metals.
(b) it gains stability due to formation of \(C_4H_4^2-\) on binding to transition metals.
(c) its polymerization ability reduces in presence of transition metal.
(d) it becomes stable in presence of transition metals due to formation of \(C_4H_4^{2+}\).

85. Identify the order representing increasing \(\pi\)-acidity of the following ligands
\(\text{C}_2\text{F}_4, \text{NEt}_3, \text{CO and C}_2\text{H}_4\)
(a) \(\text{CO < C}_2\text{F}_4 < C_2\text{H}_4 < \text{NEt}_3\)  
(b) \(C_2\text{F}_4 < C_2\text{H}_4 < \text{NEt}_3 < \text{CO}\)  
(c) \(C_2\text{H}_4 < \text{NEt}_3 < \text{CO < C}_2\text{F}_4\)  
(d) \(\text{NEt}_3 < C_2\text{H}_4 < C_2\text{F}_4 < \text{CO}\)

86. The species with highest magnetic moment (spin only value) is
(a) \(\text{VCl}_6^+\)  
(b) \(\eta^5 - C_2\text{H}_5)_2\text{Cr}\)  
(c) \(\left[\text{Co(NO}_2\right]_6^{3-}\)  
(d) \([\text{Ni(EDTA)]}^{2-}\)

87. The number of metal-metal bonds in \(\text{Ir}_2(\text{CO})_{12}\) is
(a) 4  
(b) 6  
(c) 10  
(d) 12

88. Three bands in the electronic spectrum of \(\left[\text{Cr(NH}_3\right)_6]^{3+}\) are due to the following transitions
(A) \(^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}\)  
(B) \(^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}\)  
(C) \(^4\text{A}_{2g} \rightarrow ^2\text{E}_g\)
Identify the correct statement about them
(a) Intensity of (A) is lowest  
(b) Intensity of (C) is lowest  
(c) Intensities of (A), (B) and (C) are similar  
(d) Intensities of (B) and (C) are similar

89. Identify the pairs in which the covalent radii of elements are almost similar
(A) Nb, Ta  
(B) Mo, W  
(C) La, Lu  
(D) Sc, Y
(a) A and B only  
(b) A and C only  
(c) B and C only  
(d) A, B and C only

90. Consider following lanthanide (III) ions
(A) Nd(III)  
(B) Gd(III)  
(C) Dy(III)
The magnetic moment closest to the spin only value is(are) for
(a) B only  
(b) A and B only  
(c) A and C only  
(d) B and C only

91. The \(\Delta_3\) of the following complexes
(A) \(\left[\text{CoCl}_4\right]^{2-}\)  
(B) \(\left[\text{CoBr}_4\right]^{2-}\)  
(C) \(\left[\text{Co(NCS)}_4\right]^{2-}\) follows the order
(a) C > A > B  
(b) A > B > C  
(c) B > A > C  
(d) C > B > A

92. In complexometric titration
\(S(\text{substrate}) + T(\text{titrant}) \rightarrow P(\text{product})\)
The end point is estimated spectrophotometrically. If \(S\) and \(P\) have \(\varepsilon = 0\), the shape of the titration curve would look like
\[
\begin{array}{c}
\text{(a)} \\
\text{T} \\
\uparrow A \\
\text{(b)} \\
\text{T} \\
\uparrow A
\end{array}
\]
93. Identify the chiral complexes from the following

(A) \([\text{Cr(EDTA)}]^-\)  (B) \([\text{Ru(bipy)}]^{3+}\)  (C) \([\text{PtCl(diene)}]^+\)

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

94. Distribution ratio of ‘A’ between CHCl₃ and water is 9.0. It is extracted with several, 5 mL aliquots of CHCl₃. The number of aliquots needed to extract 99.9% of ‘A’ from its 5 mL aqueous solution are

(a) 2  (b) 3  (c) 4  (d) 5

95. The correct equilibrium order for the interconversion of different forms of SiO₂ is

(a) Tridymite \(\rightleftharpoons\) quartz \(\rightleftharpoons\) cristobalite \(\rightleftharpoons\) liquid SiO₂

(b) quartz \(\rightleftharpoons\) Tridymite \(\rightleftharpoons\) cristobalite \(\rightleftharpoons\) liquid SiO₂

(c) quartz \(\rightleftharpoons\) cristobalite \(\rightleftharpoons\) tridymite \(\rightleftharpoons\) liquid SiO₂

(d) Cristobalite \(\rightleftharpoons\) tridymite \(\rightleftharpoons\) quartz \(\rightleftharpoons\) liquid SiO₂

96. The rate equation for the reaction \(2\text{AB} + \text{B}_2 \rightarrow 2\text{AB}_2\) is given by

\[
\text{rate} = k[\text{AB}][\text{B}_2] \]

A possible mechanism consistent with this rate law is

(a) \(\text{slow} \quad 2\text{AB} + \text{B}_2 \rightarrow 2\text{AB}_2\)  (b) \(\text{slow} \quad \text{AB}_2 + \text{B}_2 \rightarrow 2\text{AB}_2\)

\(\text{AB} + \text{B}_2 \rightarrow \text{AB}_3\)  (c) \(\text{fast} \quad \text{AB} + \text{AB} \rightarrow \text{A}_2\text{B}_2\)

\(\text{AB}_3 + \text{AB} \rightarrow 2\text{AB}_2\)  (d) \(\text{slow} \quad \text{AB}_4 + \text{AB} \rightarrow 2\text{AB}_2\)

97. Observe the following statements

(I) In the \(\text{H}_2\text{O}_2\) reaction, explosion occurs when the rate of chain branching exceeds that of chain termination.

(II) The order of the reaction, \(n\text{A} \rightarrow \text{products}\), is 2.5. For this reaction, \(t \propto \text{[A]}^{-2.5}\)

(III) Unimolecular gas phase reactions are second order at low pressure but becomes first order at high pressure.

Which of the following is correct?

(a) I, II and III are correct  (b) Only II is correct

(c) Only III is correct  (d) I and II are correct.
98. For the particle-in-a-box problem in \((0, L)\) an approximate wave function is given as \(x(L/2 - x)\). The average energy \(\overline{E}\) for such a state will obey

(a) \(\frac{\hbar^2}{8mL^2} < \overline{E} < \frac{\hbar^2}{2mL^2}\)  
(b) \(\overline{E} > \frac{\hbar^2}{2mL^2}\)

(c) \(\frac{\hbar^2}{4mL^2} < \overline{E} < \frac{\hbar^2}{2mL^2}\)  
(d) \(0 < \overline{E} < \frac{\hbar^2}{8mL^2}\)

99. For two variables \(x\) and \(y\), the following data set is given:

<table>
<thead>
<tr>
<th>(x)</th>
<th>(y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

The correct statement for the covariance \(A\) and correlation coefficient \(B\) of \(x\) and \(y\) is

(a) \(A = 2/3, B = 1\)  
(b) \(A = -2/3, B = 1\)  
(c) \(A = -2/3, B = -1\)  
(d) \(A = 0, B = 0\)

100. The hydrogenic orbital with the form of the radial function

\[ r^2 (\alpha_x - r)(\alpha_y - r) \exp[-\beta r], \] 

are constants, may be identified as a

(a) 3d orbital  
(b) 4f orbital  
(c) 5d orbital  
(d) 5f orbital

101. The operator \(\left[ x, \left[ x, p^2 \right] \right] \) is identical with

(a) \(\left[ px, \left[ x, p \right] \right] \)  
(b) \(\left[ xp, \left[ x, p \right] \right] \)  
(c) \(-\left[ p, \left[ x^2, p \right] \right] \)  
(d) \(\left[ x, \left[ x^2, p \right] \right] \)

102. For the particle-in-a-box problem in \((0, L)\), the value of \(\langle x^3 \rangle\) in the \(n \to \infty\) limit would be

(a) \(\frac{L^3}{6}\)  
(b) \(\frac{L^3}{3}\)  
(c) \(\frac{L^3}{4}\)  
(d) \(\frac{L^3}{4}\)

103. Identify the Mulliken notation for the following irreducible representation

\[
\begin{array}{cc|ccc|}
| E & C_n & nC_2 & i & \sigma_n | \\
| 1 & 1 & -1 & -1 & -1 |
\end{array}
\]

(a) \(A_{1u}\)  
(b) \(A_{2a}\)  
(c) \(B_{2u}\)  
(d) \(A_{2u}\)

104. Identify the point group symmetry of the following molecule (all C–C bond lengths are equal)

(a) \(C_2\)  
(b) \(S_4\)  
(c) \(D_{2d}\)  
(d) \(D_{4d}\)
105. The ground state term symbol for Nb (atomic number 41) is $^4D$. The electronic configuration corresponding to this term symbol is

(a) $[\text{Kr}]4d^3s^2$  
(b) $[\text{Kr}]4d^45s^1$  
(c) $[\text{Kr}]4d^5s^0$  
(d) $[\text{Kr}]4d^35s^15p^1$

106. In the presence of an external magnetic field (normal Zeeman effect), the transition $^1D_2 \rightarrow ^1P_1$ splits into

(a) 9 lines  
(b) 8 lines  
(c) 7 lines  
(d) 6 lines

107. Identify the Huckel determinant for cyclobutadiene

(a) $\begin{vmatrix} \alpha -E & \beta & 0 & 0 \\ \beta & \alpha -E & \beta & 0 \\ 0 & \beta & \alpha -E & \beta \\ 0 & 0 & \beta & \alpha -E \end{vmatrix}$  
(b) $\begin{vmatrix} \alpha -E & \beta & 0 & \beta \\ \beta & \alpha -E & \beta & 0 \\ 0 & \beta & \alpha -E & \beta \\ \beta & \beta & 0 & \alpha -E \end{vmatrix}$

108. On mixing 120 ml of 0.05 M CH$_3$COOH and 40 ml of 0.05 M of NaOH, the pH of the solution is

(a) $\text{pK}_a + 0.69$  
(b) $\text{pK}_a + 0.301$  
(c) $\text{pK}_a$  
(d) $\text{pK}_a - 0.69$

109. A system consists of gaseous H$_2$, O$_2$, H$_2$O and CO$_2$ where the amount of CO$_2$ is specified and the equilibrium constant for the reaction $2\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g)$ is known. The number of degrees of freedom of the system is

(a) 2  
(b) 3  
(c) 4  
(d) 5

110. “Colloids are thermodynamically unstable with reference to bulk but kinetically stable”. Identify the correct pair

**Statements**  
(A) thermodynamically unstable  
(B) kinetically stable  
(C) interfacial surface tension  
(D) electrical double layer

**Reasons**

(a) (A) $\leftrightarrow$ (D) and (B) $\leftrightarrow$ (C)  
(b) (A) $\leftrightarrow$ (C) and (B) $\leftrightarrow$ (D)  
(c) (A) $\leftrightarrow$ (C) and (B) $\leftrightarrow$ (C)  
(d) (A) $\leftrightarrow$ (D) and (B) $\leftrightarrow$ (D)

111. An AX system gave 4 lines at 4.72, 4.6, 1.12 and 1.0 ppm away from the TMS using an nmr spectrometer operating at 100 MHz. What are the values of $J_{AX}$ (in Hz) and $\delta_{AX}$ (in ppm), respectively

(a) 12 and 3.6  
(b) 6 and 3.6  
(c) 12 and 2.86  
(d) 6 and 2.86

112. The equilibrium population ratio $(n_j / n_i)$ of a doubly-degenerate energy level $(E_j)$ lying at energy 2 units higher than a lower non-degenerate energy level $(E_i)$, assuming $k_B T = 1$ unit, will be

(a) $2e^{-2}$  
(b) $2e^2$  
(c) $e^2$  
(d) $e^{-2}$
113. Which of the following statements is true for a cyclic process?
(a) \( \oint dq = 0 \)  
(b) \( \oint dw = 0 \)
(c) Heat can be completely converted into work
(d) Work can be completely converted into heat

114. Identify, from the following, the correct ionic strengths for (A) 0.01 molal solution of NaCl and (B) a 0.01 molal solution of Na\(_2\)SO\(_4\).
(a) \( A 0.010 \text{ mol kg}^{-1} \) (B) 0.010 mol kg\(^{-1}\)  
(b) \( A 0.010 \text{ mol kg}^{-1} \) (B) 0.030 mol kg\(^{-1}\)  
(c) \( A 0.010 \text{ mol kg}^{-1} \) (B) 0.025 mol kg\(^{-1}\)  
(d) \( A 0.010 \text{ mol kg}^{-1} \) (B) 0.015 mol kg\(^{-1}\)

115. A system has 100 degenerate energy levels and 100 bosons are kept in it. Find the entropy of the system at equilibrium.
(a) \( 10^{-2} \text{ k}_B \)  
(b) \( 10^2 \text{ k}_B \)  
(c) \( 460.6 \text{ k}_B \)  
(d) \( 4.606 \text{ k}_B \)

116. Which is correct Nernst equation for redox reaction \( O + ne \rightleftharpoons R \)?
(a) \( E = E^0 + \frac{RT}{nF} \ln \left[ \frac{[O]}{[R]} \right] \)  
(b) \( \frac{[O]}{[R]} = e^{\frac{nF}{RT}(E^0 - E)} \)  
(c) \( \frac{[O]}{[R]} = e^{-\frac{nF}{RT}(E - E^0)} \)  
(d) \( \frac{[O]}{[R]} = e^{\frac{RT}{nF}(E - E^0)} \)

117. A plane of spacing ‘d’ shows first order Bragg diffraction at angle \( \theta \). A plane of spacing 2d
(a) shows Bragg diffraction at 20  
(b) shows Bragg diffraction at \( \frac{\theta}{2} \)  
(c) shows Bragg diffraction at \( \sin^{-1}\left(\frac{\sin \theta}{2}\right) \)  
(d) shows Bragg diffraction at \( \sin^{-1}\left(\frac{\sin 2\theta}{2}\right) \)

118. In the formation of H\(_2\) molecules from 2H atoms placed at positions A and B, and separated by a distance \( r_{AB} \), a part of the spatial wave function is
\[ \Phi_A (1) \Phi_A (2) + \Phi_B (1) \Phi_B (2) \]
(a) This is a covalent term and is important as \( r_{AB} \to \infty \)  
(b) This is an ionic term and is important as \( r_{AB} \to \infty \)  
(c) This is a covalent term and is important as \( r_{AB} \to 0 \)  
(d) This is an ionic term and is important as \( r_{AB} \to 0 \)

119. A 0.1 M solution of compound A shows 50% transmittance when a cell of 1 cm width is used at \( \lambda_1 \) nm. Another 0.1 M solution of compound B gives the optical density value of 0.1761 using 1 cm cell at \( \lambda_1 \) nm. What will be the transmittance of a solution that is simultaneously 0.1 M in A and 0.1 M in B using the same cell and at the same wave length?
[log 20 = 1.301; log 30 = 1.4771; log 50 = 1.699]
(a) 33.3%  
(b) 50%  
(c) 66.7%  
(d) 70%
120. Using standard equation for intrinsic viscosity \([\eta] = K M^a_v\), for a solution of polymer and any information from the graph identify viscosity average molar mass \(\langle M \rangle\) [given that \(a = 0.5, K = 5 \times 10^{-5} \text{ L g}^{-1}\)]

\[
\frac{\eta - \eta_0}{\eta_0} = \frac{1}{c}
\]

(a) \(10^3 \text{ g/mol}\)  
(b) \(10^4 \text{ g/mol}\)  
(c) \(10^5 \text{ g/mol}\)  
(d) \(10^6 \text{ g/mol}\)

121. Among the following, the correct statement for the following reaction is

![Reaction diagram](image)

(a) A is the major product and it will have five signals in the proton decoupled \(^{13}\text{C}\) NMR spectrum  
(b) A is the minor product and it will have eight signals in the proton decoupled \(^{13}\text{C}\) NMR spectrum  
(c) B is the major product and it will have five signals in the proton decoupled \(^{13}\text{C}\) NMR spectrum  
(d) B is the minor product and it will have five signals in the proton decoupled \(^{13}\text{C}\) NMR spectrum

122. For the following three step conversion of A to B, the appropriate sequence of reactions is

![Conversion diagram](image)

(a) \(\text{MnO}_2; (\text{CH}_2\text{OH})_2/p-\text{TSA}; \text{PCC}\)  
(b) \(\text{PCC}; \text{MnO}_2; (\text{CH}_2\text{OH})_2/p-\text{TSA}\)  
(c) \(\text{PCC}; (\text{CH}_2\text{OH})_2/p-\text{TSA}; \text{Jones’ reagent}\)  
(d) \(\text{Jones’ reagent}; (\text{CH}_2\text{OH})_2/p-\text{TSA}; \text{MnO}_2\)

123. Which one of the following statements is true for the following transformation?

![Transformation diagram](image)

(a) A is the major product and it is a Cram product.  
(b) A is the major product and it is anti-Cram product.  
(c) B is the major product and it is a Cram product.  
(d) B is the major product and it is anti-Cram product.
124. Which one of the following statements is true for the following transformation?

(a) Suitable reagent is m-CPBA and B is the major product.
(b) Suitable reagent in m-CPBA and A is the major product.
(c) Suitable reagent is aq. $\text{H}_2\text{O}_2$/NaOH and B is the major product.
(d) Suitable reagent is aq. $\text{H}_2\text{O}_2$/NaOH and A is the major product.

125. The compound formed in the following reaction sequence is

1. Li, liq. $\text{NH}_3$, t-BuOH
2. 10% aq. $\text{H}_2\text{SO}_4$

126. Among the following compounds, the one which has highest dipole moment is

127. In the UV-visible spectrum, a diterpenoid exhibited a $\lambda_{\text{max}}$ at 275 nm. The compound, among the choices given below is
128. The major product formed in the following reaction is

\[ \text{CH}_2=\text{CH} + \text{CH}_2=\text{NO}_2 \xrightarrow{1. \Delta} \xrightarrow{2. \text{TiCl}_3, \text{HCl}} \]

(a) \[\text{(c)}\] (b) \[\text{(d)}\] (c) \[\text{(a)}\] (d) \[\text{(b)}\]

129. In the broad band decoupled $^{13}$C NMR spectrum, the number of signals appearing for the two pyrene-diols A and B

(a) eight and eight  (b) eight and sixteen  (c) five and ten  (d) five and eight.

130. An organic compound exhibited the following $^1$H NMR spectra data:

$\delta$ 7.80 (2 H, d, $J = 8$ Hz), 6.80 (2 H, d, $J = 8$ Hz), 4.10 (2H, q, $J = 7.2$ Hz), 2.4 (3H, s), 1.25 (3 H, t, $J = 7.2$ Hz)

The compound, among the choices given below is,

(a) \[\text{(a)}\] (b) \[\text{(b)}\] (c) \[\text{(c)}\] (d) \[\text{(d)}\]
131. $\alpha$-Pinene on reaction with dilute alkaline $\text{KMnO}_4$ produces a diol, which on further oxidation with chromium trioxide gives product A, which undergoes a positive haloform test. The compound A is

$$\begin{align*}
\text{(a)} & \quad \text{O} \\
\text{(b)} & \quad \text{COOH} \\
\text{(c)} & \quad \text{COOH} \\
\text{(d)} & \quad \text{O} 
\end{align*}$$

132. The major product formed in the reaction of guanosine with one equivalent of methyl iodide is

$$\begin{align*}
\text{(a)} & \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{O} \\
\text{(b)} & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{O} \\
\text{(c)} & \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{O} \\
\text{(d)} & \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{O} 
\end{align*}$$

133. The major product formed in the following reaction is

$$\begin{align*}
\text{(a)} & \quad \text{O} \\
\text{(b)} & \quad \text{O} \\
\text{(c)} & \quad \text{O} \\
\text{(d)} & \quad \text{O} 
\end{align*}$$

134. Reaction of the dipeptide, given below, with hydrogen in the presence of 10% palladium over carbon, produces a mixture of

$$\begin{align*}
\text{(a)} & \quad \text{Gly-Leu + toluene + carbon dioxide} \\
\text{(b)} & \quad \text{Phe-Leu + toluene + carbon dioxide} \\
\text{(c)} & \quad \text{Phe-Leu + benzyl alcohol + carbon dioxide} \\
\text{(d)} & \quad \text{Gly-Leu + benzyl alcohol + carbon dioxide} 
\end{align*}$$
135. Among the following, the most suitable reagent for carrying out resolution of racemic 3-methylcyclohexanone is

- (a) \( \text{OH} \)
- (b) \( \text{Ph} \text{H} \text{OH} \)
- (c) \( \text{MeOOC} \text{H} \text{COO} \text{Me} \)
- (d) \( \text{O} \text{H} \text{H} \text{O} \)

136. In the following reaction sequence, structures of the major product X and Y are

\[
\text{C}_6\text{H}_4\text{NO}_2 + (\text{COOEt})_2 \xrightarrow{\text{NaOEt}} \text{X} \xrightarrow{\text{Zn/AcOH}} \text{Y}
\]

- (a) X is \( \text{X} \text{is} \text{Y} \text{is} \text{Y} \)
- (b) X is \( \text{X} \text{is} \text{Y} \text{is} \text{Y} \)
- (c) X is \( \text{X} \text{is} \text{Y} \text{is} \text{Y} \)
- (d) X is \( \text{X} \text{is} \text{Y} \text{is} \text{Y} \)

137. Consider the following reaction sequence

\[
\begin{align*}
\text{Ph} \xrightarrow{\text{Sn/HCl (90%)}} \text{Ph} & \xrightarrow{\text{Ac}_2\text{O (90%)}} \text{AcCHN} \\
\text{Ph} & \xrightarrow{\text{HNO}_3 (25%)} \text{Ph} & \xrightarrow{\text{Sn/HCl (90%)}} \text{Ph} & \xrightarrow{\text{Ac}_2\text{O (90%)}} \text{Ph}
\end{align*}
\]
The overall yield for the formation of p-hydroxyacetanilide and o-hydroxyacetanilides from phenol, respectively, are approximately
(a) 57 and 20%  (b) 57 and 68%  (c) 83 and 68%  (d) 83 and 20%

138. The most stable conformations of 1, 2-difluoroethane and dl-2, 3-butanediol are

139. Reaction of (S)-1, 2, 4-butanetriol with benzaldehyde in the presence of catalytic amount of p-TSA furnished the major product A. The structure of A is

140. The major product formed in the following reaction is

141. The major product formed in the following reaction is
142. The major product formed in the following reaction is

\[ \text{N}_2 \xrightarrow{1. \text{hv, aq. THF}} \] 
\[ \xrightarrow{2. \Delta} \]

![Chemical structure](image)

(a) (b) (c) (d)

143. The major product formed in the following reaction is

![Chemical structure](image)

144. Predict the condition A and the structure of the major product B in the following sequence.

\[ \xrightarrow{\text{A}} \] 
\[ \xrightarrow{1. \text{O}_3; \text{Me}_2\text{S}} \] 
\[ \xrightarrow{2. \text{Ph}_3\text{P = CHCOOEt (excess)}} \]

(a) A is hv, B is (b) A is hv, B is (c) A is Δ, B is (d) A is Δ, B is
145. The most appropriate mode of cyclisation in the following transformation is

(a) con-rotatory in photochemical; and dis-rotatory in thermal conditions.
(b) con-rotatory in thermal; and dis-rotatory in photochemical conditions.
(c) con-rotatory in thermal; and con-rotatory in photochemical conditions.
(d) dis-rotatory in photochemical; and dis-rotatory in thermal conditions.