

PART-B
CHEMISTRY

51. For a ligand substitution reaction, which statement about the volume of activation is correct?
- (A) A large negative value of ΔV^\ddagger indicates an associative mechanism
- (B) A large positive value of ΔV^\ddagger indicates an associative mechanism
- (C) A large negative value of ΔV^\ddagger indicates a dissociative mechanism
- (D) Values of ΔV^\ddagger cannot be used to distinguish between associative and dissociative mechanism.
52. The average residence time for a water molecule in the first coordination sphere of $[\text{Cs}(\text{OH}_2)_8]^+$ is approximately 10^{-10} seconds. The value of water exchange rate constant is, therefore:
- (A) 10^{-10} s
- (B) 10^{10} s⁻¹
- (C) 10^{-10} s⁻¹
- (D) 10^{10} s
53. In an inner-sphere electron transfer reaction, which of the following ligands could not act as a bridging ligand?
- (A) 1, 10 phenanthroline
- (B) 4, 4'-bipyridine
- (C) pyrazine
- (D) bis (4-pyridyl) methane
54. Racemization of a chiral complex $[\text{Cr}(\text{ox})_3]^{3-}$ is least likely to occur by
- (A) a dissociative pathway
- (B) a pathway involving a 5-coordinate species in which one ox^{2-} ligand is monodentate
- (C) the Ray-Dutt twist mechanism
- (D) the Bailar twist mechanism
55. Which of the following has a center of inversion?
- (i) CO_2
- (ii) C_2H_2
- (iii) BF_3
- (iv) SO_4^{2-}
- (A) (i) and (ii) only
- (B) (i) and (iii) only
- (C) (i) and (iv) only
- (D) (ii) and (iii) only
56. Addition of bismuth chloride to an excess of water produces
- (A) Clear solution
- (B) Yellow solution
- (C) White precipitate
- (D) Orange-red precipitate
57. Monochromatic X-rays having a wavelength of 10.4 \AA are preferentially diffracted by a crystal at an angle of 25.5° , assuming that this is the first order diffraction with a d-spacing between crystalline planes equal to 12.1 \AA . What is the value of $\sin \theta$ for the angle for the second-order diffraction?
- (A) 0.959
- (B) 0.759
- (C) 0.859
- (D) 0.659

58. Which of the following order is correct for the scattering of X-rays?
- (A) $F < O < Cl < Na < Tl$
 (B) $F < Cl < Na < O < Tl$
 (C) $O < Cl < F < Na < Tl$
 (D) $O < F < Na < Cl < Tl$
59. The p^5 electronic configuration is equivalent to the term
- (A) 3P
 (B) 2P
 (C) 3F
 (D) 4P
60. Which of the following structures represents the conjugate acid of HPO_4^{2-} ?
- (A) $H_2PO_4^-$
 (B) H_3PO_4
 (C) $H_4PO_4^+$
 (D) PO_4^{3-}
61. A buffer solution contains ethanoic acid and its conjugate base; the pK_a of ethanoic acid is 4.74. At what pH does the solution buffer?
- (A) 3.0
 (B) 4.0
 (C) 5.0
 (D) 6.0
62. A student recorded a polarogram of 2.0 mM Cd^{2+} solution but forgot to add KCl solution. What type of error can you expect in these results.
- (A) Only migration current will be observed
 (B) Only diffusion current will be observed
 (C) Both migration current as well as diffusion current will be observed
 (D) Both catalytic current, as well as diffusion current will be observed.
63. Pick the correct statement about atomic emission spectroscopy from the following
- (i) Hg lamp is not a suitable source for AAS
 (ii) Graphite furnace is the best atomizer for AAS
 (iii) Non-metals cannot be determined by AAS
 (iv) AAS is better than ICP-AES for simultaneous determination of metals
- (A) (i), (ii) and (iii)
 (B) (ii), (iii) and (iv)
 (C) (iii), (iv) and (i)
 (D) (iv), (i) and (ii)
64. The low temperature ($-98^\circ C$) ^{19}F NMR spectrum of SF_4 shows doublets of triplets. It is consistent with the point group symmetry
- (A) C_{3v}
 (B) C_{4v}
 (C) T_d
 (D) C_{2v}

65. Which of the following spectroscopic techniques will be useful to distinguish between M-SCN and M-NCS binding modes?

- (A) NMR
- (B) IR
- (C) EPR
- (D) Mass

66. The total numbers of fine and hyperfine EPR lines expected for an octahedral high spin Mn(II) complexes are respectively ($I = 5/2$ for Mn)

- (A) 3 and 30
- (B) 5 and 33
- (C) 5 and 30
- (D) 4 and 24

67. Match reaction in List I with intermediates List II and select the correct answer using the codes given below :

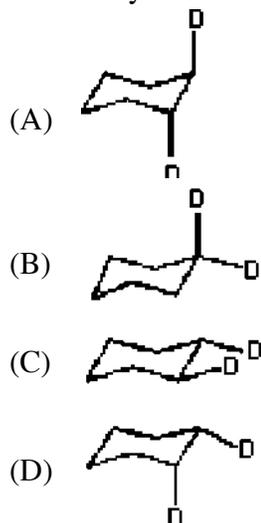
- | List-I | List-II |
|--------------------|---------------------------|
| a. Friedel -Crafts | 1. Nitrene intermediate |
| b. Cannizaro | 2. Carbanion intermediate |
| c. Hofmann | 3. Hydride transfer |
| d. Dieckmann | 4. Arenium ion |

- (A) a-3, b-4, c-2, d-1
- (B) a-4, b-3, c-1, d-2
- (C) a-2, b-3, c-1, d-4
- (D) a-1, b-2, c-3, d-4

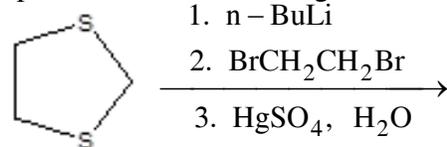
68. Reaction of 1-pentene with NBS (N-bromosuccinimide) forms two isomeric bromopentenes, one of which is 3-bromo-1-pentene. Which of the following is the other isomer?

- (A) 1-bromo-2-pentene.
- (B) 5-bromo-1-pentene.
- (C) 1-bromo-1-pentene.
- (D) 2-bromo-1-pentene.

69. The major product obtained by the addition of D_2 to cyclohexene in presence of a catalyst is

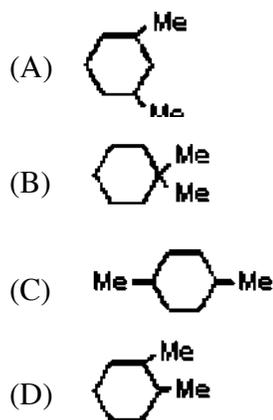


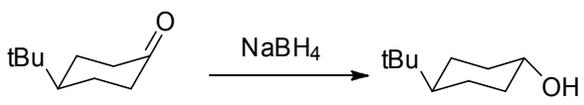
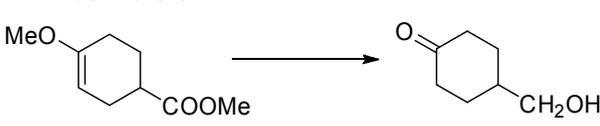
70. The product in the following reaction is



- (A) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$
- (B) $\text{OHCCH}_2\text{CH}_2\text{CHO}$
- (C) Cyclopropane
- (D) Glyoxal (OHCCHO)

71. The CMR spectrum of an unknown compound shows 4 absorptions and the PMR spectrum also shows 4 absorptions. Identify the compound?



72. The Kiliani-Fischer reaction of an aldopentose
- is a diastereoselective reaction
 - is an enantioselective reaction
 - gives a mixture of aldohexoses differing in configuration at C_6 .
 - gives a racemic mixture
73. Treatment of 1-methylcyclohexene with an ether solution of diborane (B_2H_6), followed by reaction with alkaline H_2O_2 gives
- 1-methylcyclohexanol
 - cis*-1-methylcyclohexane-1,2-diol
 - cis*-2-methylcyclohexanol
 - trans*-2-methylcyclohexanol
74. Photolysis of an aliphatic ketone with molecular formula $C_8H_{16}O$ gives ethylene, propylene, n-butyl methyl ketone and n-propyl methyl ketone besides two cyclobutanol derivatives. The ketone is likely to be
- 4-octanone
 - 3-octanone
 - 2-octanone
 - n-propyl t-butyl ketone
75. Which of the following synthon represents the structure $RCOCH = CH_2$?
- $RCH(OH)CH_2^+$
 - $RCH_2CH_2^+$
 - $RCOCH_2CH_2^+$
 - $RCOCH_2^+$
76. Which of the following is least aromatic ?
- Pyrrole
 - Furan
 - Pyridine
 - Thiophene
77. Which of the following statements is not correct?
- Glycerol stearate can be used to prepare sodium soaps.
 - Estradiol is a steroid while insulin is a protein
 - All amines give diazonium salts on treatment with aqueous HNO_2 . (ans)
 - 2-Pentanol gives positive iodoform test.
78. The following reaction is an example of
- 
- The reaction shows a cyclohexanone ring with a tert-butyl group at the 4-position. The carbonyl group is at the 1-position. It reacts with $NaBH_4$ to form a cyclohexanol ring with a tert-butyl group at the 4-position and a hydroxyl group at the 1-position.
- Regioselectivity
 - Chemoselectivity
 - Stereoselectivity
 - Stereospecificity
79. Which of the following is not a solution for Green chemistry?
- Catalysis
 - Efficient energy techniques
 - Low atom economy
 - Recyclable solvents
80. Mark the correct reagent for the following conversion:
- 
- The reaction shows a cyclohexene ring with a methoxy group (MeO) at the 1-position and a methyl ester group ($COOMe$) at the 4-position. It is converted to a cyclohexanone ring with a carbonyl group at the 1-position and a hydroxymethyl group (CH_2OH) at the 4-position.
- $NaBH_4$ followed by H_3O^+
 - H_3O^+ followed by $NaBH_4$
 - $LiAlH_4$ followed by H_3O^+
 - H_3O^+ followed by $LiAlH_4$

81. The following reaction can be classified as
- 
- (A) Cycloaddition
 (B) Cope rearrangement
 (C) Retro Diels-Alder reaction
 (D) Electrocyclic reaction
82. Which of the following reactions does not use Pd as a reagent?
 (A) Negishi Coupling
 (B) Stille Coupling
 (C) McMurry reaction
 (D) Sonagashira reaction
83. Using an appropriate supramolecular host, it is possible to bind which of the following hosts ?
 (A) Neutral species
 (B) Cations
 (C) Anions
 (D) All of these
84. An octapeptide has the composition Ala₂, Gly₂, Phe₂, Ser₂. The N-terminal unit is Ala. Cleavage of the octapeptide by chymotrypsin gives a single tetrapeptide, having Ala as its N-terminal group. Among the products of random hydrolysis is a Phe-Ala-Gly tripeptide fragment. What is the primary structure of the octapeptide?
 (A) Ala-Gly-Ser-Phe-Phe-Ser-Gly-Ala
 (B) Ala-Ser-Gly-Phe-Ala-Gly-Ser-Phe
 (C) Ala-Ser-Gly-Phe-Ala-Ser-Gly-Phe
 (D) Ala-Gly-Ser-Phe-Ala-Gly-Ser-Phe
85. The reaction of ethyl formate with excess of C₂H₅MgBr gives
 (A) Diethyl ketone
 (B) Ethyl methyl ketone
 (C) 2-Propanol
 (D) 2-Pentanol
86. The slope of the curve between log T vs log V in a reversible adiabatic expansion of a gas is
 (A) 1 - γ
 (B) γ - 1
 (C) γ
 (D) (1 - γ)⁻¹
 (where γ = c_p / c_v)
87. The ratio of zero point energy of H-D to H-H (assuming the force constant is same and the mass of deuterium is twice that of hydrogen) is
 (A) 1.15
 (B) 0.869
 (C) 1.42
 (D) 0.706
88. The expression for thermal de Broglie wavelength is
 (A) (h²β/2πm)^{1/2}
 (B) h³β/(2πm)^{1/2}
 (C) (2πm/hβ)^{1/2}
 (D) (hβ²/2πm)^{1/2}

89. Which of the following relation is not correct?

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

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

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

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

90. If the dissociation constant of HCN and CH_3COOH are 4×10^{-10} M and 1.8×10^{-5} M respectively. The pH of a solution containing NaCN would be ----- the pH of a solution containing same amount of CH_3COONa

- (A) Larger than
 (B) Smaller than
 (C) Equal to
 (D) Smaller or equal to

91. The ground state term symbol for Pd atom with electronic configuration $[\text{Kr}](4d)^{10}$ is

- (A) 1S_0
 (B) $^2S_{1/2}$
 (C) $^2P_{1/2}$
 (D) 2S_0

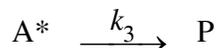
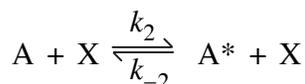
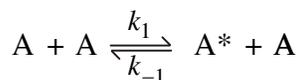
92. When d^2/dx^2 operates on the function $6 \sin(4x)$, we find

- (A) The function is an eigenfunction with eigenvalue -96
 (B) The function is an eigenfunction with eigenvalue 16
 (C) The function is an eigenfunction with eigenvalue -16
 (D) The function is not an eigenfunction

93. In the conductometric titration of silver nitrate against potassium chloride

- (A) The conductance increases sharply till the end point
 (B) The conductance decreases sharply till the end point
 (C) The conductance remains more or less same till the end point
 (D) The conductance decreases sharply after the end point

94. In the given Lindemann mechanism of unimolecular decomposition of 'A' in presence of an inert molecule 'X'



On applying SSA, the rate law for the formation of product is

(A) $r = \frac{k_3(k_1[x]^2 + k_2[A][X])}{k_{-1}[A] + k_{-2}[X] + k_3}$

(B) $r = \frac{k_1(k_1[A]^2 + k_2[A][X])}{k_{-1}[A] + k_{-2}[X] + k_3}$

(C) $r = \frac{k_3(k_1[A]^2 + k_2[A][X])}{k_{-1}[X] + k_{-2}[A] + k_3}$

(D) $r = \frac{k_3(k_1[A]^2 + k_2[A][X])}{k_{-1}[A] + k_{-2}[X] + k_3}$

95. In the first order perturbation theory of particle in a one dimensional box from $x = 0$ to $x = a$ with a slanted bottom such that

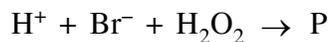
$$V(x) = \frac{V_0 x}{a} \quad 0 \leq x \leq a$$

The first order correction term in the energy will be

- (A) V_0
 (B) $V_0/2$
 (C) $V_0/4$
 (D) $2V_0$

(Given $\int_0^a x \sin^2(n\pi x/a) dx = a^2/4$)

96. For the given ionic reaction



The plot of $\ln(k/k_0)$ versus $I^{1/2}$ will be

- (A) Straight line with positive slope
 (B) Straight line with negative slope
 (C) Straight line parallel to $I^{1/2}$ axis
 (D) The variation is not a straight line

97. In the Huckel theory of conjugated π -electron system, the roots of secular determinants of ethene molecule is/are

- (A) $E = \alpha \pm \beta$
 (B) $E = \alpha - 2\beta$
 (C) $E = \alpha \pm \sqrt{2}\beta$
 (D) $E = \alpha + 2\beta$

98. Gold (atomic mass 197 g/mol) crystallizes as face centered cubic lattice. The approximate number of unit cells present in 1 g of gold is

- (A) 3.05×10^{21}
 (B) 6.02×10^{23}
 (C) 7.64×10^{20}
 (D) 3.05×10^{23}

99. The mean of four determinations of the Iron content of a sample of an alloy was 8.27% with a standard deviation $s = 0.17\%$. With 95% confidence limit (the t value for 95% confidence level with 3 degrees of freedom is 3.18), the true value of the Iron content of the alloy lies in the range of

- (A) 8.0% to 8.54%
 (B) 7.83% to 8.71%
 (C) 7.0% to 7.75%
 (D) 8.0% to 8.88%

100. The point groups present in trichloromethane and Nitrogen trifluoride are respectively

- (A) C_{2v} and C_{2v}
 (B) C_{2v} and C_{3v}
 (C) C_{3v} and C_{2v}
 (D) C_{3v} and C_3

ROUGH WORK

Answer Key: Chemistry

51	a
52	b
53	a
54	a
55	a
56	c
57	c
58	d
59	b
60	a
61	c
62	c
63	a
64	d
65	b
66	c
67	b
68	a
69	d
70	b
71	d
72	a
73	d
74	a
75	c
76	b
77	c
78	c
79	c
80	c
81	d
82	c
83	d
84	c
85	d
86	a
87	b
88	a
89	c
90	a
91	a
92	c
93	c
94	d
95	b
96	b
97	a
98	c
99	a
100	d