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CHEMICAL SCIENCES

PART-B

- For an octahedral Cu²⁺ complex depicting axial EPR spectrum $(g_{\parallel} > g_{\perp})$, the geometry of Cu²⁺ and 21. the orbital containing the unpaired electron are, respectively
 - (a) Tetragonally elongated, $d_{x^2-y^2}$ (b) Tetragonally compressed, d_{z^2}
 - (d) Tetragonally compressed, $d_{x^2-y^2}$ (c) Tetragonally elongated, d_{z^2}
- 22. The major product formed in the following reaction is



23. The correct match of ¹³C NMR chemical shift values (δppm) for pyridine is



(a) C2:136; C3:124; C4:150 (c) C2:150; C3:124; C4:136

(b) C2:124; C3:150; C4:136 (d) C2:150; C3:136; C4:124

- 24. Molar composition of a mixture of P and Q at equilibrium is 3:1 (P:Q). A small disturbance in composition results in change of chemical potential of P by 10 J mol⁻¹. The chemical potential of Q will change (in J mol⁻¹) by: (b) 3.3 (a) 30 (c) - 30(d) - 3.3
- 25. E1cb mechanism is followed in the reaction of
 - (a) 2-bromopentane with t-BuOK to give pent-2-ene
 - (b) nitromethane with benzaldehyde in the presence of KOH to give β -nitrostyrene
 - (c) bormobenzene with NaNH₂ to give aniline
 - (d) p-chloronitrobenzene with NaOMe to give p-nitroanisole



26. For the complex shown below in non-fluxional state, the expected ³¹P {¹H} NMR resonance(s) is/are $\begin{bmatrix} {}^{31}P:I = \frac{1}{2} \end{bmatrix}$



- (a) one singlet (b) one doublet (c) two singlets (d) two doublets
 27. The value of a physical variable was found to be 196, 198, 194, 199 and 198 in a set of five independent measurements. The average value and the standard deviation would be closest, respectively to (a) 198 and 2 (b) 197 and 4 (c) 197 and 2 (d) 198 and 4
 28. The frequency of O-H stretch occurs at ~3600 cm⁻¹. The O-D stretch frequency (in cm⁻¹)
- (a) 3000 (b) 2600 (c) 1800 (d) 900
- 29. The major product formed in the following reaction is





34. The major product formed in the following reaction is



- A liquid of density 1.1g cm⁻³ climbs to a height of 5.0 cm when a capillary with internal radius of 0.2 mm is dipped into it. The surface tension (in Nm⁻¹) of the liquid is closest to (a) 0.05 (b) 0.108 (c) 0.018 (d) 0.005
- 36. The expected number of v_{CO} bands in the IR spectra of fac-[Mo(PPh₃)₃(CO)₃] and *trans*-[Mo(PPh₃)₂(CO)₄] are, respectively. (a) one and one (b) two and two (c) two and one (d) three and one
- 37. The pair of light source and atomizer resulting highest sensitivity to atomic asborption spectrometric measurement is
 - (a) Hg lamp; nitric oxide flame (b) Hg lamp; graphite furnace
 - (c) Hollow cathode lamp; graphite furnace (d) Hollow cathode lamp; acetylene-nitric oxide flame
- 38. The major product formed in the following reaction is



39. Consider the entropy changes in a system undergoing transformation, as depicted in the diagram, below



The correct statement among the following is

- (a) $\Delta S_1 = \Delta S_2$ and $\Delta S \neq \Delta S_1 + \Delta S_2$ (b) $\Delta S_1 > \Delta S_2$ and $\Delta S \neq \Delta S_1 + \Delta S_2$ (c) $\Delta S_1 = \Delta S_2$ and $\Delta S = \Delta S_1 + \Delta S_2$ (d) $\Delta S_1 > \Delta S_2$ and $\Delta S = \Delta S_1 + \Delta S_2$
- 40. The most stable vanadium species in aqueous medium is
 - (a) $\left[V(H_2O)_5(OH) \right]^{2+}$ (b) $\left[VO(H_2O)_5 \right]^{2+}$ (c) $\left[VO(H_2O)_5 \right]^{+}$ (d) $\left[V(H_2O)_4(OH)_2 \right]^{2+}$



- The common heptacity observed for coordination of C_{60} to a metal center is 41. (a) 2(b) 4(c) 5(d) 6
- Choose the correct statements for oxymyoglobin and cytochrome P_{450} (resting state) from the following 42. (A) Both contain dianion of protoporphyrin-IX
 - (B) They have same fifth-ligand bonded to metal centre from the protein backbone
 - (C) They contain single active site
 - (D) They contain metal ion in +3 oxidation state
 - Answer is

- 43. In common glass electrode, alkaline error caused at pH > 10 is least for (a) 0.01 M NaCl (c) 1.0 M LiCl (b) 1.0 M NaCl (d) 1.0 M KCl
- 44. A cube does not have the symmetry element (b) C_{3} (a) C_{γ} (c) C_{A} (d) C_{6}
- 45. The correct order for the rate of thermal decarboxylation of the following compound is



Pair of lanthanide ions which show significant deviation between the experimental and calculated 46. magnetic moments, considering contribution from the ground state only (Given:

$$\mu_{eff} = g [J(J+1)]^{1/2}$$
] is

(a) Gd^{3+} and Lu^{3+}

(b) Sm^{3+} and Tb^{3+}

(c) Eu^{3+} and Tb^{3+}

- (d) Sm^{3+} and Eu^{3+}
- If the rate constant for a base catalyzed estser hydrolysis reaction is 0.20 L mol⁻¹ s⁻¹, half-life (in 47. s) of the ester (Given [ester]_o = [base]_o = 0.05 mol. L^{-1}] would be closest to (a) 40 (b) 100[°] (c) 140 (d) 200
- 48. The major product formed in the following reaction is







53. Consider four species A, B, C and D

$$A + B \xrightarrow{KI, H^+} C$$

Oxidation of A with C in an acidic medium gives D, A, B, C and D are, respectively



- (a) $S_4O_6^{2-}$, I_2 , KIO_3 and SO_4^{2-} (b) $S_4O_6^{2-}$, KIO_3 , I_2 and SO_4^{2-} (c) $S_2O_3^{2-}$, KIO_3 , I_2 and $S_4O_6^{2-}$ (d) $S_2O_3^{2-}$, KIO_3 , I_2 and SO_4^{2-}
- 54. The major product formed in the following reaction is



- 55. Correct order of molar extinction coefficient values of the visible absorption bands for the following species is
 - (a) $\left[\operatorname{Cr} \left(\operatorname{H}_{2} \operatorname{O} \right)_{6} \right]^{2+} > \left[\operatorname{Mn} \left(\operatorname{H}_{2} \operatorname{O} \right)_{6} \right]^{2+} > \operatorname{Chlorophyll} > \left[\operatorname{NiCl}_{4} \right]^{2-}$
 - (b) Chlorophyll > $[NiCl_4]^{2^-} > [Cr(H_2O)_6]^{2^+} > [Mn(H_2O)_6]^{2^+}$
 - (c) $[\operatorname{NiCl}_4]^{2-}$ > Chlorophyll > $[\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_6]^{2+}$ > $[\operatorname{Mn}(\operatorname{H}_2\operatorname{O})_6]^{2+}$
 - (d) Chlorophyll > $\left[Cr(H_2O)_6 \right]^{2+}$ > $\left[NiCl_4 \right]^{2-}$ > $\left[Mn(H_2O)_6 \right]^{2+}$ Consider a two-level system in which the excited state, separated from the ground state by energy ε ,
 - is doubly degenerate. The fraction of the molecules in the excited state, as $T \rightarrow \infty$, is

(a)
$$\frac{1}{3}$$
 (b) $\frac{1}{2}$ (c) $\frac{2}{3}$ (d) 1
. Identify from following, the products of K-electron capture by the nucleus
(A) neutron (B) neutrino (C) positron
Answer is
(a) A only (b) A and B (c) C only (d) B and C

58. In IR spectrum, recorded neat, a compound shows a strong and broad band at 3300 cm⁻¹. The band becomes sharp and shifts to 3600 cm⁻¹ when the spectrum is recorded in CCl₄ at high dilution. This proves that the compound has
(a) OU snown, which is invested in intermedeevelop U handing.

(a) OH group, which is involved in intramolecular H-bonding

56.

57



- (b) OH group, which is involved in intermolecular H-bonding
- (c) a terminal alkyne group
- (d) OH group, present in severely sterically hindered environment
- 59. TRUE statement for the following transformation is



- (a) ΔH^0 and ΔS^0 are positive (b) ΔH^0 and ΔS^0 are negative
- (c) ΔH^0 is positive and ΔS^0 is negative (d) ΔH^0 is negative and ΔS^0 is positive
- 60. The correct match for the drug molecules in the Column-A with their medicinal use in Column-B is Column-A Column-B





PART - C Match the items in Column-I with those of Column-II 61. **Column-I** (species) **Column-II** (structure/properties) (A) NaH (I) polymeric chain (B) BeH₂ (II) interstitial hydride (C) $HfH_{2.10}$ (D) $[TcH_{0}]^{2-10}$ (III) tricapped trigonal prismatic (IV) saline hydride The correct match is (a) A-IV, B-II, C-III, D-I (b) A-I, B-IV, C-II, D-III (c) A-IV, B-I, C-II, D-III (d) A-IV, B-I, C-III, D-II 62. In a polymer of N monomer units, the root mean square separation between the two ends is (a) $N^{1/2}$ (c) $N^{3/2}$ (d) N^2 (b) N 63. The rate-determining step in the catalytic synthesis of acetic acid by Monsanto process is (a) Oxidative addition of CH_3I to $\left[RhI_2(CO)_2\right]^{-1}$ (b) Migration of CH_3 group to CO of $[RhI_3(CO)_2(CH_3)]$ (c) Loss of CH₃COI from $\left[RhI_3(CO)_2(COCH_3) \right]^{-1}$ (d) Coordination of CO to $[RhI_3CO(COCH_3)]^-$ 64. TRUE statement regarding Hammett reaction constant (ρ) for the following transformations given in equations A and B is Θ 000. CO₂Et НΟ **EtOH** (Equation A) ⊖ 000. CO₂Et e но **EtOH** (Equation B) (a) ρ for A and B is same and positive (b) ρ for A and B is same and negative (c) ρ for A is larger positive value than for B (d) ρ for A is negative and for B is positive 65. The major product formed in the following reaction is Et (i) CHCl₃, KOH (ii) H₂O₂, NaOH HC (b) HO Et (a) HOEt

OH

HC







72. The correct absolute configuration of the following compounds is



73. Consider the gas phase reaction, $2A(g)+3B(g) \Longrightarrow 2C(g)$ at a given temperature. When 2.0 moles of A(g) are reacted with 2.0 moles of B(g), 0.8 moles of C(g) are formed at equilibrium at a total pressure of 2.0 bar. The value of the equilibrium constant, K_p of this reaction at the given temperature is closest to
(a) 0.3 (b) 0.9 (c) 2.4 (d) 19.1

74. 1.0 mol of a perfect monatomic gas is put through the cycle shown in the figure. The total work (in J) done during the cycle is (Use: 1L-bar = 100 J, R = 8.3 JK⁻¹ mol⁻¹ = 0.083 L-bar K⁻¹ mol⁻¹, ln 2 = 0.7)



(a) 930 (b) -4183 (c) 8831 (d) -5113

75. Among $SO_2(OH)F$, CH_3CO_2H , LiF and H_2O , the compound(s) which behave(s) as a base in liquid HF is/are

(a) CH ₃ CO ₂ H and LiF only	(b) LiF only
(c) $SO_2(OH)F$ and LiF only	(d) CH_3CO_2H , LiF and H_2O
The meder residual entropy (in IV-1) of	askid OCC would be also at to

- 76. The molar residual entropy (in JK⁻¹) of solid OCS would be closest to (a) 0 (b) 2.9 (c) 5.8 (d) 8.7
- 77. The structure of the compound, which displays the following spectral data is IR = 1690, 1100 cm⁻¹ ¹H NMR : $\delta 2.8(s, 3H)$, 3.8(s, 3H), 6.9(d, J = 8 Hz, 2H), 7.8(d, J = 8 Hz, 2H)¹³C NMR : $\delta 197, 165, 130, 129, 114, 56, 26$





- 78. In the pure rotational microwave spectrum of a XY molecule, the adjacent lines are separated by 4 cm⁻¹. If the molecule is irradiated by a radiation of 30, 000 cm⁻¹, the first Stokes line (in cm⁻¹) appears at
 - (a) 29988 (b) 30012 (c) 30004 (d) 29996
- 79. The spatial part of the dominant resonance structure of the LiH molecule is (only valance part of the wavefunction is shown)

(a)
$$2s_{Li}(r_1) 2s_{Li}(r_2)$$

(b)
$$2s_{Li}(r_1)2s_H(r_2)+2s_{Li}(r_2)1s_H(r_1)$$

- (c) $2s_{Li}(r_1) ls_H(r_2) 2s_{Li}(r_2) ls_H(r_1)$ (d) $ls_H(r_1) ls_H(r_2)$
- FeCr₂O₄ and NiGa₂O₄ have normal and inverse spinel structures, respectively. The correct statement 80.
 - (a) Fe(II) and Ni(II) occupy octahedral sites
 - (b) Fe(II) and Ni(II) occupy tetrahedral and octahedral sites, respectively
 - (c) Cr(III) and Ga(III) occupy only octahedral sites
 - (d) Cr(III) and Ga(III) occupy tetrahedral and octahedral sites, respectively
- 81.

For the reaction $K + Br_2 \rightarrow KBr + Br$, which follows the harpoon mechanism, the reactive cross-section is closest to Given: $\frac{e^2}{4\pi\epsilon_0} = 2.3 \times 10^{-28} \text{ J m}$, Ionization energy of of $K = 422.5 \text{ kJmol}^{-1}$, electron affinity of $Br_2 = 250 \text{ kJ mol}^{-1}$ and $N_A = 6 \times 10^{23} \text{ mol}^{-1}$

(b) $2 \times 10^{-18} \text{ m}^2$ (c) $64 \times 10^{-18} \text{ m}^2$ (d) $16 \times 10^{-18} \text{ m}^2$ (a) $50 \times 10^{18} \text{ m}^2$

- 82. For the electrochemical cell Ag | AgCl | MCl (0.01 M) | MCl(0.02 M) | AgCl | Ag, the junction potential is the highest when M⁺ is (c) Na^+ (d) K^{+} (a) H^{+} (b) Li^+
- In the electronic spectrum of [IrBr_e]²⁻, the number of charge transfer band(s) and their origin are, 83. respectively
 - (a) Two, ligand \rightarrow metal $(\sigma \rightarrow t_{2g} \text{ and } \sigma \rightarrow a_{1g}^*)$
 - (b) One, ligand \rightarrow metal $(\sigma \rightarrow e_g)$
 - (c) Two, ligand \rightarrow metal ($\sigma \rightarrow t_{2g}$ and $\sigma \rightarrow e_{g}$)



- (d) One, ligand \rightarrow metal $(\sigma \rightarrow t_{2g})$
- 84. The major product formed in the following reaction is



- 86. X-rays of 173 pm wavelength are reflected by the (111) plane of a cubic primitive crystal at $\theta = 30^{\circ}$. The unit cell length (in pm) is closest to (a) 173 (b) 300 (c) 346 (d) 600
- 87. The major product formed in the following reaction is







88. $(C_P - C_V)$ for a non-ideal gas differes from $(C_P - C_V)$ for a perfect gas by the expression

(a) $\left(\frac{\partial P}{\partial T}\right)_{V} \left(\frac{\partial U}{\partial P}\right)_{S}$	(b) $\left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}}\right)_{\mathbf{P}} \left(\frac{\partial \mathbf{U}}{\partial \mathbf{V}}\right)_{\mathbf{T}}$	(c) $-\frac{1}{T} \left(\frac{\partial V}{\partial T} \right)_{P} \left(\frac{\partial U}{\partial V} \right)_{T}$	$(d) \left(\frac{\partial P}{\partial T}\right)_{V} \left(\frac{\partial U}{\partial T}\right)_{P}$
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89. The main product of nucleophilic attack of H^- on the complex ion given below is



- 90. The order of a surface catalyzed unimolecular reaction, at very low and very high pressures of the reactant, would be respectively.
 (a) 0, 0
 (b) 1, 0
 (c) 0, 1
 (d) 1, 1
- 91. The major product formed in the following reaction is





- 92. The degeneracy of the state having energy $\frac{27h^2}{8mL^2}$ for a particle in a 3-D cubic box of length L is (a) 4 (b) 3 (c) 2 (d) 1
- 93. The major products A and B in the following reaction sequence are



94. The function, which is **NOT** an eigenfunction of the indicated operator, is **Operator Function Operator Function**

- (a) $\frac{d^2}{dx^2} x^2$ $e^{-x^2/2}$ (b) $\frac{d^2}{dx^2} + x^2$ $e^{-x^2/2}$ (c) $\frac{d^2}{dx^2}$ $\cos \frac{\pi x}{4}$ (d) $\frac{d^2}{dx^2}$ e^{4ix}
- 95. Choose the equilibria from the following that are NOT favoured to go to right.
 - (A) $As_2S_5 + 5HgO \Longrightarrow As_2O_5 + 5HgS$ (B) $La_2(CO_3)_3 + Bi_2S_3 \Longrightarrow La_2S_3 + Bi_2(CO_3)_3$ (C) $CdSO_4 + CaS \Longrightarrow CdS + CaSO_4$ (D) $BeF_2 + HgI_2 \Longrightarrow BeI_2 + HgF_2$ (a) A and B (b) A and C (c) B and C (d) B and D



- 96. In spectrofluorimetric determination in solution
 - (A) absorbance of analyte solution is kept near to 0.05
 - (B) oxygen is eradicated from solution
 - (C) pH of solution is controlled
 - (D) wavelength of incident light is always above 400 nm
 - Correct from the above is
 - (a) A, B and D (b) B, C and D (c) A, B and C (d) A, C and D
- 97. The major product formed in the following reaction is



98. Products (A) and (B) formed in the following transformation of alkylidenecarbenes are







- 99. The correct match of spin-only magnetic moment for the complexes cis-[Fe(phen)₂(NCS-N)₂] (A) and [Fe(phen)₃]Cl₂ (B) at 300K is (phen = 1, 10-phenanthroline) (a) 4.89 BM for both A and B (c) 4.89 BM for A and 0 BM for B (d) 0 BM for A and 4.89 BM for B
- 100. The Hückel molecular orbital of benzene that is degenerate with the molecular orbital

$$\frac{1}{2}(\chi_{2} + \chi_{3} - \chi_{5} - \chi_{6}), \text{ is}$$
(a) $\frac{1}{\sqrt{12}}(2\chi_{1} + \chi_{2} - \chi_{3} - 2\chi_{4} - \chi_{5} + \chi_{6})$
(b) $\frac{1}{2}(\chi_{2} - \chi_{3} + \chi_{5} - \chi_{6})$
(c) $\frac{1}{\sqrt{12}}(2\chi_{1} - \chi_{2} - \chi_{3} + 2\chi_{4} - \chi_{5} - \chi_{6})$
(d) $\frac{1}{\sqrt{6}}(\chi_{1} - \chi_{2} + \chi_{3} - \chi_{4} + \chi_{5} - \chi_{6})$

101. The reducible representation, Γ , in the table is equal to the following superposition of the irreducible representation of C_{2v} point group.

C _{2V}	Е	C ₂	$\sigma_{\rm V}$	σ'_{V}
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1
Γ	8	-2	-6	4

(a) $A_1 \oplus 2A_2 \oplus 5B_1$ (b) $A_1 \oplus 2A_2 \oplus 5B_2$ (c) $5A_1 \oplus A_2 \oplus 2B_1$ (d) $A_1 \oplus 5A_2 \oplus 2B_2$



- 102. The correct statements for dithionite and dithionate anions from the following are
 - (A) both have S-S bond
 - (B) both are dianionic
 - (C) oxidation state of sulphur is +3 and +5, respectively
 - (D) sulphur in dithionate has lone pair of electrons
 - (a) A, B and C (b) A, B and D (c) B, C and D (d) A and B only
- 103. The major product A and the byproducts B formed in the following reaction are







TiCl₄

108. The major product formed in the following reaction is

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112. The intermediate A and the major product (B) formed in the following reaction are





113. The major products (A) and (B) formed in the following reactions are



114. The intermediate (A) and the major product (B) formed in the following reaction are







115. Consider the following statements:
(A) The highest oxidation state of Group 8 elements is more readily shown in their oxides than in fluorides
(B) Fe can exist in -2 formal oxidation state also
(C) Mn, Tc and Re easily form M(II) compounds

The correct statement(s) is/are

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

- 116. The species for which the shapes (geometry) can be predicted by VSEPR theory is/are
 - (A) $[PtCl_4]^{2-}$ (B) $[TeCl_6]^{2-}$ (C) PF_3 and SF_6 (a) A and C (b) B and C (c) C only (d) A and B
- 117. The correct order of the reactions involved in the following transformation is



- (a) Michael addition, Quasi-Favorskii rearrangement, Aldol condensation
- (b) Quasi-Favorskii rearrangement, Michael addition, Aldol condensation
- (c) Michael addition, Aldol condensation, Quasi-Favorskii rearrangement
- (d) Aldol condensation, Quasi-Favorskii rearrangement, Michael addition



118. The compound that shows peaks in the EI mass spectrum at m/z 121, 105, 77, 44 is



119. The correct order of metal-carbon distance is

(a)
$$\operatorname{Fe}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Co}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Ni}(\eta^{5}-\operatorname{Cp})_{2}$$
 (b) $\operatorname{Fe}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Ni}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Co}(\eta^{5}-\operatorname{Cp})_{2}$
(c) $\operatorname{Ni}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Fe}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Co}(\eta^{5}-\operatorname{Cp})_{2}$ (d) $\operatorname{Ni}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Co}(\eta^{5}-\operatorname{Cp})_{2} > \operatorname{Fe}(\eta^{5}-\operatorname{Cp})_{2}$

120. The rate constant of a second order reaction $2A \rightarrow Z$ is k_2 . If the initial concentration of the reactant is a_0 and the concentration of the product at time *t* is *x*, then a linear function of t with the slope k_2a_0 is

(a)
$$\ln\left(\frac{x}{a_0 - x}\right)$$
 (b) $\frac{x}{a_0(a_0 - x)}$ (c) $\frac{x}{a_0 - x}$ (d) $\ln\left(\frac{x}{a_0(a_0 - x)}\right)$
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