## PAPER : CSIR-UGC-NET/JRF DEC. 2019 <br> CHEMICAL SCIENCES

## PART-B

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

(a)

(b)

(c)

(d)

23. The correct match of ${ }^{13} \mathrm{C}$ NMR chemical shift values ( $\delta \mathrm{ppm}$ ) for pyridine is

(a) C2:136; C3:124; C4:150
(b) C2:124; C3:150; C4:136
(c) C2:150; C3:124; C4:136
(d) C2:150; $\mathrm{C} 3: 136 ; \mathrm{C} 4: 124$
24. Molar composition of a mixture of P and Q at equilibrium is $3: 1(\mathrm{P}: \mathrm{Q})$. A small disturbance in composition results in change of chemical potential of P by $10 \mathrm{~J} \mathrm{~mol}^{-1}$. The chemical potential of Q will change (in $\mathrm{J} \mathrm{mol}^{-1}$ ) by:
(a) 30
(b) 3.3
(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 $\beta$-nitrostyrene
(c) bormobenzene with $\mathrm{NaNH}_{2}$ to give aniline
(d) $p$-chloronitrobenzene with NaOMe to give $p$-nitroanisole
26. For the complex shown below in non-fluxional state, the expected ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR resonance(s) is/are

$$
\left[{ }^{31} \mathrm{P}: I=1 / 2\right]
$$


(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 $\mathrm{O}-\mathrm{H}$ stretch occurs at $\sim 3600 \mathrm{~cm}^{-1}$. The $\mathrm{O}-\mathrm{D}$ stretch frequency (in $\mathrm{cm}^{-1}$ )
(a) 3000
(b) 2600
(c) 1800
(d) 900
29. The major product formed in the following reaction is

30. The ion having the highest bond order is
(a) $\mathrm{NO}^{+}$
(b) $\mathrm{O}_{2}^{+}$
(c) $\mathrm{N}_{2}{ }^{+}$
(d) $\mathrm{C}_{2}{ }^{+}$

31. $\quad \bullet \quad \bullet \quad \bullet \quad \bullet \quad \bullet$| $\bullet$ | $\bullet$ | $\bullet$ | $\bullet$ |
| :---: | :---: | :---: | :---: |
| $\bullet$ | $\bullet$ | $\bullet$ | $\bullet$ |
| $\bullet$ | $\bullet$ | $\bullet$ | $\bullet$ |
|  | $\bullet$ |  |  |

The Miller- index for the plane as shown in the figure and parallel to the c-axis, is
(a) 110
(b) 120
(c) 210
(d) 220
32. The cell potential (in V ) of a $\mathrm{Ag} / \mathrm{AgCl} / \mathrm{KCl}$ electrode connected to the standard hydrogen electrode at 298 K is closest to (Given: $\mathrm{E}_{\left(\mathrm{AgCl} / \mathrm{AgCl}^{-}\right)}^{0}=0.222 \mathrm{~V}$ and assume that the activity of KCl is 0.01 )
(a) 0.197
(b) 0.297
(c) 0.340
(d) 0.440
33. The titration of 4.4 g of a polymer having carboxylic acid end group requires 11 mL of 0.02 M NaOH . The average molar mass (in $\mathrm{kg} \mathrm{mol}^{-1}$ ) of the polymmer is
(a) 40
(b) 20
(c) 15
(d) 10
34. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

35. A liquid of density $1.1 \mathrm{~g} \mathrm{~cm}^{-3}$ 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 $\mathrm{Nm}^{-1}$ ) of the liquid is closest to
(a) 0.05
(b) 0.108
(c) 0.018
(d) 0.005
36. The expected number of $v_{\mathrm{Co}}$ bands in the IR spectra of fac- $\left[\mathrm{Mo}\left(\mathrm{PPh}_{3}\right)_{3}(\mathrm{CO})_{3}\right]$ and trans$\left[\mathrm{Mo}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{CO})_{4}\right]$ 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

(a)

(b)

(c)

(d)

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


The correct statement among the following is
(a) $\Delta \mathrm{S}_{1}=\Delta \mathrm{S}_{2}$ and $\Delta \mathrm{S} \neq \Delta \mathrm{S}_{1}+\Delta \mathrm{S}_{2}$
(b) $\Delta \mathrm{S}_{1}>\Delta \mathrm{S}_{2}$ and $\Delta \mathrm{S} \neq \Delta \mathrm{S}_{1}+\Delta \mathrm{S}_{2}$
(c) $\Delta \mathrm{S}_{1}=\Delta \mathrm{S}_{2}$ and $\Delta \mathrm{S}=\Delta \mathrm{S}_{1}+\Delta \mathrm{S}_{2}$
(d) $\Delta \mathrm{S}_{1}>\Delta \mathrm{S}_{2}$ and $\Delta \mathrm{S}=\Delta \mathrm{S}_{1}+\Delta \mathrm{S}_{2}$
40. The most stable vanadium species in aqueous medium is
(a) $\left[\mathrm{V}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}(\mathrm{OH})\right]^{2+}$
(b) $\left[\mathrm{VO}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{2+}$
(c) $\left[\mathrm{VO}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{+}$
(d) $\left[\mathrm{V}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})_{2}\right]^{2+}$
41. The common heptacity observed for coordination of $\mathrm{C}_{60}$ to a metal center is
(a) 2
(b) 4
(c) 5
(d) 6
42. Choose the correct statements for oxymyoglobin and cytochrome $\mathrm{P}_{450}$ (resting state) from the following
(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
(a) A, B and C
(b) A, C and D
(c) A, B and D
(d) B and C only
43. In common glass electrode, alkaline error caused at $\mathrm{pH}>10$ is least for
(a) 0.01 M NaCl
(b) 1.0 M NaCl
(c) 1.0 M LiCl
(d) 1.0 M KCl
44. A cube does not have the symmetry element
(a) $\mathrm{C}_{2}$
(b) $\mathrm{C}_{3}$
(c) $\mathrm{C}_{4}$
(d) $\mathrm{C}_{6}$
45. The correct order for the rate of thermal decarboxylation of the following compound is

(a) $\mathrm{C}>$ B $>\mathrm{A}$
(b) C $>$ A $>$ B
(c) A $>$ C $>$ B
(d) B $>$ C $>$ A
46. Pair of lanthanide ions which show significant deviation between the experimental and calculated magnetic moments, considering contribution from the ground state only (Given: $\left.\mu_{e f f}=g[J(J+1)]^{1 / 2}\right]$ is
(a) $\mathrm{Gd}^{3+}$ and $\mathrm{Lu}^{3+}$
(b) $\mathrm{Sm}^{3+}$ and $\mathrm{Tb}^{3+}$
(c) $\mathrm{Eu}^{3+}$ and $\mathrm{Tb}^{3+}$
(d) $\mathrm{Sm}^{3+}$ and $\mathrm{Eu}^{3+}$
47. If the rate constant for a base catalyzed estser hydrolysis reaction is $0.20 \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$, half-life (in s) of the ester (Given [ester] $\left.{ }_{o}=[\text { base }]_{o}=0.05 \mathrm{~mol} \mathrm{~L}^{-1}\right]$ would be closest to
(a) 40
(b) 100
(c) 140
(d) 200
48. The major product formed in the following reaction is


(a)

(b)

(c)

(d)

49. The correct order of basicity of the following anions is

(A)
(B)
(C)
(D)
(a) B $>$ A $>$ C $>$ D
(b) $\mathrm{D}>\mathrm{B}>\mathrm{C}>\mathrm{A}$
(c) $\mathrm{C}>\mathrm{D}>\mathrm{B}>\mathrm{A}$
(d) B $>$ A $>$ D $>$ C
50. The major product formed in the following reaction is
(a)

(a)


(b)


(c)

(d)

51. The hydrogen atomic orbital given by $N r^{2} e^{-r / 3 a_{0}}\left(3 \cos ^{2} \theta-1\right)$ represents
(a) $2 p$ orbitals
(b) 3 p orbital
(c) 3d orbital
(d) 4 d orbital
52. The magnitude of bond angles in gaseous $\mathrm{NF}_{3}, \mathrm{SbF}_{3}$ and $\mathrm{SbCl}_{3}$ follow the order
(a) $\mathrm{NF}_{3}>\mathrm{SbF}_{3}>\mathrm{SbCl}_{3}$
(b) $\mathrm{SbCl}_{3}>\mathrm{SbF}_{3}>\mathrm{NF}_{3}$
(c) $\mathrm{SbF}_{3}>\mathrm{SbCl}_{3}>\mathrm{NF}_{3}$
(d) $\mathrm{NF}_{3}>\mathrm{SbCl}_{3}>\mathrm{SbF}_{3}$
53. Consider four species A, B, C and D

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

Oxidation of A with C in an acidic medium gives $\mathrm{D}, \mathrm{A}, \mathrm{B}, \mathrm{C}$ and D are, respectively
(a) $\mathrm{S}_{4} \mathrm{O}_{6}^{2-}, \mathrm{I}_{2}, \mathrm{KIO}_{3}$ and $\mathrm{SO}_{4}^{2-}$
(b) $\mathrm{S}_{4} \mathrm{O}_{6}^{2-}, \mathrm{KIO}_{3}, \mathrm{I}_{2}$ and $\mathrm{SO}_{4}^{2-}$
(c) $\mathrm{S}_{2} \mathrm{O}_{3}^{2-}, \mathrm{KIO}_{3}, \mathrm{I}_{2}$ and $\mathrm{S}_{4} \mathrm{O}_{6}^{2-}$
(d) $\mathrm{S}_{2} \mathrm{O}_{3}^{2-}, \mathrm{KIO}_{3}, \mathrm{I}_{2}$ and $\mathrm{SO}_{4}^{2-}$
54. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

55. Correct order of molar extinction coefficient values of the visible absorption bands for the following species is
(a) $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}>\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}>$ Chlorophyll $>\left[\mathrm{NiCl}_{4}\right]^{2-}$
(b) Chlorophyll $>\left[\mathrm{NiCl}_{4}\right]^{2-}>\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}>\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
(c) $\left[\mathrm{NiCl}_{4}\right]^{2-}>$ Chlorophyll $>\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}>\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
(d) Chlorophyll $>\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}>\left[\mathrm{NiCl}_{4}\right]^{2-}>\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
56. Consider a two-level system in which the excited state, separated from the ground state by energy $\varepsilon$, is doubly degenerate. The fraction of the molecules in the excited state, as $\mathrm{T} \rightarrow \infty$, is
(a) $\frac{1}{3}$
(b) $\frac{1}{2}$
(c) $\frac{2}{3}$
(d) 1
57. 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 $3300 \mathrm{~cm}^{-1}$. The band becomes sharp and shifts to $3600 \mathrm{~cm}^{-1}$ when the spectrum is recorded in $\mathrm{CCl}_{4}$ at high dilution. This proves that the compound has
(a) OH group, which is involved in intramolecular H -bonding
(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) $\Delta \mathrm{H}^{0}$ and $\Delta \mathrm{S}^{0}$ are positive
(b) $\Delta \mathrm{H}^{0}$ and $\Delta \mathrm{S}^{0}$ are negative
(c) $\Delta \mathrm{H}^{0}$ is positive and $\Delta \mathrm{S}^{0}$ is negative
(d) $\Delta \mathrm{H}^{0}$ is negative and $\Delta \mathrm{S}^{0}$ 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
(P)
(Q)

Warfarin
(R)

(III) Antibiotic
(a) P-I; Q-II; R-III
(b) P-II; Q-I; R-III
(c) P-III; Q-I; R-II
(d) P-I; Q-III; R-II

## PART - C

61. Match the items in Column-I with those of Column-II

## Column-I (species)

(A) NaH
(B) $\mathrm{BeH}_{2}$
(C) $\mathrm{HfH}_{2}$
(D) $\left[\mathrm{TcH}_{9}\right]^{2-}$

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) $\mathrm{N}^{1 / 2}$
(b) N
(c) $\mathrm{N}^{3 / 2}$
(d) $\mathrm{N}^{2}$
63. The rate-determining step in the catalytic synthesis of acetic acid by Monsanto process is
(a) Oxidative addition of $\mathrm{CH}_{3} \mathrm{I}$ to $\left[\mathrm{RhI}_{2}(\mathrm{CO})_{2}\right]$
(b) Migration of $\mathrm{CH}_{3}$ group to CO of $\left[\mathrm{RhI}_{3}(\mathrm{CO})_{2}\left(\mathrm{CH}_{3}\right)\right]^{-}$
(c) Loss of $\mathrm{CH}_{3} \mathrm{COI}$ from $\left[\mathrm{RhI}_{3}(\mathrm{CO})_{2}\left(\mathrm{COCH}_{3}\right)\right]^{-}$
(d) Coordination of CO to $\left[\mathrm{RhI}_{3} \mathrm{CO}\left(\mathrm{COCH}_{3}\right)\right]^{-}$
64. TRUE statement regarding Hammett reaction constant $(\rho)$ for the following transformations given in equations A and B is


(a) $\rho$ for A and B is same and positive
(b) $\rho$ for A and B is same and negative
(c) $\rho$ for A is larger positive value than for B
(d) $\rho$ for A is negative and for B is positive
65. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

66. The cluster types of $\left[\mathrm{Fe}_{5}(\mathrm{CO})_{14} \mathrm{~N}\right]^{-}$and $\left[\mathrm{Co}_{6}(\mathrm{CO})_{13} \mathrm{~N}\right]^{-}$are, respectively
(a) nido-, nido-
(b) nido-, closo-
(c) closo-, nido-
(d) closo-, closo-
67. Match the items in Column-I with those of Column-II

Column-I
(A) Conductometric titration
(B) Amperometric titrations
(C) pH metric titration
(D) Differential pulse polarography

Correct match is
(a) A-II, B-IV, C-I, D-III
(b) A-III, B-I, C-II, D-IV
(c) A-III, B-II, C-IV, D-I
(d) A-I, B-III, C-IV, D-II
68. Complex(es) which has/have unpaired electron(s) that is equal to that of iron center in oxymyoglobin is/are
(A) $\left[\mathrm{Fe}(\mathrm{ox})_{3}\right]^{3-}$
(B) $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$
(C) $\left[\mathrm{NiCl}_{4}\right]^{2-}$
(D) $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$
[Given: ox = oxalato]
Correct answer is
(a) A and B
(b) B and D
(c) C only
(d) C and D
69. In Mössbauer spectrum of a sample containing iron recorded in the presence of a static magnetic field, the number of possible allowed transitions(s) is
(a) Two
(b) Four
(c) Six
(d) Eight
70. The oxidation of NO to $\mathrm{NO}_{2}$ occurs via the mechanism given below

$$
2 \mathrm{NO} \underset{\mathrm{k}_{-1}}{\stackrel{\mathrm{k}_{1}}{\rightleftharpoons}} \mathrm{~N}_{2} \mathrm{O}_{2} ; \quad \mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} \xrightarrow{\mathrm{k}_{2}} 2 \mathrm{NO}_{2}
$$

$\frac{\mathrm{d}\left[\mathrm{NO}_{2}\right]}{\mathrm{dt}}$ in the presence of large excess of $\mathrm{O}_{2}$ can be written as
(a) $2 \mathrm{k}_{1}(\mathrm{NO})^{2}$
(b) $2 \mathrm{k}_{1} \mathrm{k}_{2}(\mathrm{NO})^{2}\left(\mathrm{O}_{2}\right)$
(c) $\frac{\mathrm{k}_{1}}{\mathrm{k}_{2}}(\mathrm{NO})^{2}$
(d) $2 \mathrm{k}_{2}(\mathrm{NO})^{2}$
71. In linear variation method using two orthogonal basis functions, the two roots obtained are $\epsilon_{0}$ and $\epsilon_{1}\left(\epsilon_{0}<\epsilon_{1}\right)$. The correct relation of these with exact ground and first excited state energies, $E_{0}$ and $E_{1}$, respectively, is
(a) $\epsilon_{0} \geq E_{0}$ and $\epsilon_{1}<E_{1}$
(b) $\epsilon_{0}<\mathrm{E}_{1}$ and $\epsilon_{1} \geq \mathrm{E}_{1}$
(c) $\epsilon_{0}<\mathrm{E}_{0}$ and $\epsilon_{1}<\mathrm{E}_{1}$
(d) $\epsilon_{0} \geq \mathrm{E}_{0}$ and $\epsilon_{1} \geq \mathrm{E}_{1}$
72. The correct absolute configuration of the following compounds is

(I)

(II)
(a) I:M; II:R
(b) I:M; II:S
(c) I:P; II: R
(d) I:P; II:S
73. Consider the gas phase reaction, $2 \mathrm{~A}(\mathrm{~g})+3 \mathrm{~B}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{C}(\mathrm{g})$ at a given temperature. When 2.0 moles of $\mathrm{A}(\mathrm{g})$ are reacted with 2.0 moles of $\mathrm{B}(\mathrm{g}), 0.8$ moles of $\mathrm{C}(\mathrm{g})$ are formed at equilibrium at a total pressure of 2.0 bar. The value of the equilibrium constant, $\mathrm{K}_{\mathrm{p}}$ 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: $\left.1 \mathrm{~L}-\mathrm{bar}=100 \mathrm{~J}, \mathrm{R}=8.3 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}=0.083 \mathrm{~L}-\mathrm{bar} \mathrm{K}^{-1} \mathrm{~mol}^{-1}, \ln 2=0.7\right)$

(a) 930
(b) -4183
(c) 8831
(d) -5113
75. Among $\mathrm{SO}_{2}(\mathrm{OH}) \mathrm{F}, \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}, \mathrm{LiF}$ and $\mathrm{H}_{2} \mathrm{O}$, the compound(s) which behave(s) as a base in liquid HF is/are
(a) $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ and LiF only
(b) LiF only
(c) $\mathrm{SO}_{2}(\mathrm{OH}) \mathrm{F}$ and LiF only
(d) $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$, LiF and $\mathrm{H}_{2} \mathrm{O}$
76. The molar residual entropy (in $\mathrm{JK}^{-1}$ ) 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 $\mathrm{IR}=1690,1100 \mathrm{~cm}^{-1}$ ${ }^{1} \mathrm{H}$ NMR : $\delta 2.8(\mathrm{~s}, 3 \mathrm{H}), 3.8(\mathrm{~s}, 3 \mathrm{H}), 6.9(\mathrm{~d}, \mathrm{~J}=8 \mathrm{~Hz}, 2 \mathrm{H}), 7.8(\mathrm{~d}, \mathrm{~J}=8 \mathrm{~Hz}, 2 \mathrm{H})$
${ }^{13}$ C NMR : $\delta 197,165,130,129,114,56,26$
(a)

(b)

(c)

(d)

78. In the pure rotational microwave spectrum of a XY molecule, the adjacent lines are separated by 4 $\mathrm{cm}^{-1}$. If the molecule is irradiated by a radiation of $30,000 \mathrm{~cm}^{-1}$, the first Stokes line (in $\mathrm{cm}^{-1}$ ) 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) $2 \mathrm{~s}_{\mathrm{Li}}\left(\mathrm{r}_{1}\right) 2 \mathrm{~s}_{\mathrm{Li}}\left(\mathrm{r}_{2}\right)$
(b) $2 \mathrm{~s}_{\mathrm{Li}}\left(\mathrm{r}_{1}\right) 2 \mathrm{~s}_{\mathrm{H}}\left(\mathrm{r}_{2}\right)+2 \mathrm{~s}_{\mathrm{Li}}\left(\mathrm{r}_{2}\right) 1 \mathrm{~s}_{\mathrm{H}}\left(\mathrm{r}_{1}\right)$
(c) $2 \mathrm{~s}_{\mathrm{Li}}\left(\mathrm{r}_{1}\right) 1 \mathrm{~s}_{\mathrm{H}}\left(\mathrm{r}_{2}\right)-2 \mathrm{~s}_{\mathrm{Li}}\left(\mathrm{r}_{2}\right) 1 \mathrm{~s}_{\mathrm{H}}\left(\mathrm{r}_{1}\right)$
(d) $1 \mathrm{~s}_{\mathrm{H}}\left(\mathrm{r}_{1}\right) 1 \mathrm{~s}_{\mathrm{H}}\left(\mathrm{r}_{2}\right)$
80. $\mathrm{FeCr}_{2} \mathrm{O}_{4}$ and $\mathrm{NiGa}_{2} \mathrm{O}_{4}$ have normal and inverse spinel structures, respectively. The correct statement is
(a) Fe (II) and $\mathrm{Ni}(\mathrm{II})$ 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) $\mathrm{Cr}($ III ) and Ga (III) occupy tetrahedral and octahedral sites, respectively
81. For the reaction $\mathrm{K}+\mathrm{Br}_{2} \rightarrow \mathrm{KBr}+\mathrm{Br}$, which follows the harpoon mechanism, the reactive crosssection is closest to (Given: $\frac{\mathrm{e}^{2}}{4 \pi \varepsilon_{0}}=2.3 \times 10^{-28} \mathrm{~J} \mathrm{~m}$, Ionization energy of of $\mathrm{K}=422.5 \mathrm{kJmol}^{-1}$, electron affinity of $\mathrm{Br}_{2}=250 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $\mathrm{N}_{\mathrm{A}}=6 \times 10^{23} \mathrm{~mol}^{-1}$
(a) $50 \times 10^{18} \mathrm{~m}^{2}$
(b) $2 \times 10^{-18} \mathrm{~m}^{2}$
(c) $64 \times 10^{-18} \mathrm{~m}^{2}$
(d) $16 \times 10^{-18} \mathrm{~m}^{2}$
82. For the electrochemical cell $\mathrm{Ag}|\mathrm{AgCl}| \mathrm{MCl}(0.01 \mathrm{M})|\mathrm{MCl}(0.02 \mathrm{M})| \mathrm{AgCl} \mid \mathrm{Ag}$, the junction potential is the highest when $\mathrm{M}^{+}$is
(a) $\mathrm{H}^{+}$
(b) $\mathrm{Li}^{+}$
(c) $\mathrm{Na}^{+}$
(d) $\mathrm{K}^{+}$
83. In the electronic spectrum of $\left[\operatorname{IrBr}_{6}\right]^{2-}$, the number of charge transfer band(s) and their origin are, respectively
(a) Two, ligand $\rightarrow$ metal $\left(\sigma \rightarrow \mathrm{t}_{2 \mathrm{~g}}\right.$ and $\left.\sigma \rightarrow \mathrm{a}_{1 \mathrm{~g}}^{*}\right)$
(b) One, ligand $\rightarrow$ metal $\left(\sigma \rightarrow \mathrm{e}_{\mathrm{g}}\right)$
(c) Two, ligand $\rightarrow$ metal $\left(\sigma \rightarrow \mathrm{t}_{2 \mathrm{~g}}\right.$ and $\left.\sigma \rightarrow \mathrm{e}_{\mathrm{g}}\right)$
(d) One, ligand $\rightarrow$ metal $\left(\sigma \rightarrow \mathrm{t}_{2 \mathrm{~g}}\right)$
84. The major product formed in the following reaction is

(i) HBr
(ii) $\mathrm{MeOH}, \mathrm{H}^{+}$
$\xrightarrow[\text { (iii) } \mathrm{MeP}(\mathrm{OEt})_{2}]{ }$
(iv) $\mathrm{H}_{3} \mathrm{O}^{+}$
(a)

(b)

(c)

(d)

85. The major product of the following reaction is

(a)

(b)

(c)

(d)

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

(a)

(b)

(c)

(d)

88. $\quad\left(C_{P}-C_{V}\right)$ for a non-ideal gas differes from $\left(C_{P}-C_{V}\right)$ for a perfect gas by the expression
(a) $\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{P}}\right)_{\mathrm{S}}$
(b) $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$
(c) $-\frac{1}{\mathrm{~T}}\left(\frac{\partial \mathrm{~V}}{\partial \mathrm{~T}}\right)_{\mathrm{P}}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$
(d) $\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}\left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$
89. The main product of nucleophilic attack of $\mathrm{H}^{-}$on the complex ion given below is


(a)
(b)



(d)

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

(a)

(b)

(c)

(d)

92. The degeneracy of the state having energy $\frac{27 \mathrm{~h}^{2}}{8 \mathrm{~mL}^{2}}$ 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

(a) $\mathrm{A}=$


(b) $\mathrm{A}=$


(c) $\mathrm{A}=$

$B=$

(d) $\mathrm{A}=$


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

Operator Function
(a) $\frac{d^{2}}{d x^{2}}-x^{2}$
$e^{-x^{2} / 2}$
(b) $\frac{d^{2}}{d x^{2}}+x^{2} \quad e^{-x^{2} / 2}$
(c) $\frac{d^{2}}{d x^{2}}$
$\cos \frac{\pi x}{4}$
(d) $\frac{d^{2}}{d x^{2}}$
$e^{4 i x}$
95. Choose the equilibria from the following that are NOT favoured to go to right.
(A) $\mathrm{As}_{2} \mathrm{~S}_{5}+5 \mathrm{HgO} \rightleftharpoons \mathrm{As}_{2} \mathrm{O}_{5}+5 \mathrm{HgS}$
(B) $\mathrm{La}_{2}\left(\mathrm{CO}_{3}\right)_{3}+\mathrm{Bi}_{2} \mathrm{~S}_{3} \rightleftharpoons \mathrm{La}_{2} \mathrm{~S}_{3}+\mathrm{Bi}_{2}\left(\mathrm{CO}_{3}\right)_{3}$
(C) $\mathrm{CdSO}_{4}+\mathrm{CaS} \rightleftharpoons \mathrm{CdS}+\mathrm{CaSO}_{4}$
(D) $\mathrm{BeF}_{2}+\mathrm{HgI}_{2} \rightleftharpoons \mathrm{BeI}_{2}+\mathrm{HgF}_{2}$
(a) A and B $\quad$ (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

(a)

(b)

(c)

(d)

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


(a) $\mathrm{A}=$


(b) $\mathrm{A}=$
 $B=$

(c) $\mathrm{A}=$


(d) $\mathrm{A}=$


99. The correct match of spin-only magnetic moment for the complexes cis-[Fe(phen) $\left.)_{2}(\mathrm{NCS}-\mathrm{N})_{2}\right](\mathbf{A})$ and $\left[\mathrm{Fe}(\text { phen })_{3}\right] \mathrm{Cl}_{2}(\mathbf{B})$ at 300 K is (phen $=1,10$-phenanthroline)
(a) 4.89 BM for both A and B
(b) 0 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 $\frac{1}{2}\left(\chi_{2}+\chi_{3}-\chi_{5}-\chi_{6}\right)$, is
(a) $\frac{1}{\sqrt{12}}\left(2 \chi_{1}+\chi_{2}-\chi_{3}-2 \chi_{4}-\chi_{5}+\chi_{6}\right)$
(b) $\frac{1}{2}\left(\chi_{2}-\chi_{3}+\chi_{5}-\chi_{6}\right)$
(c) $\frac{1}{\sqrt{12}}\left(2 \chi_{1}-\chi_{2}-\chi_{3}+2 \chi_{4}-\chi_{5}-\chi_{6}\right)$
(d) $\frac{1}{\sqrt{6}}\left(\chi_{1}-\chi_{2}+\chi_{3}-\chi_{4}+\chi_{5}-\chi_{6}\right)$
101. The reducible representation, $\Gamma$, in the table is equal to the following superposition of the irreducible representation of $C_{2 v}$ point group.

| $\mathrm{C}_{2 \mathrm{~V}}$ | E | $\mathrm{C}_{2}$ | $\sigma_{\mathrm{v}}$ | $\sigma^{\prime}{ }_{\mathrm{v}}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{A}_{1}$ | 1 | 1 | 1 | 1 |
| $\mathrm{~A}_{2}$ | 1 | 1 | -1 | -1 |
| $\mathrm{~B}_{1}$ | 1 | -1 | 1 | -1 |
| $\mathrm{~B}_{2}$ | 1 | -1 | -1 | 1 |
|  |  |  |  |  |
| $\Gamma$ | 8 | -2 | -6 | 4 |

(a) $\mathrm{A}_{1} \oplus 2 \mathrm{~A}_{2} \oplus 5 \mathrm{~B}_{1}$
(b) $\mathrm{A}_{1} \oplus 2 \mathrm{~A}_{2} \oplus 5 \mathrm{~B}_{2}$
(c) $5 \mathrm{~A}_{1} \oplus \mathrm{~A}_{2} \oplus 2 \mathrm{~B}_{1}$
(d) $\mathrm{A}_{1} \oplus 5 \mathrm{~A}_{2} \oplus 2 \mathrm{~B}_{2}$
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

(a) $\mathrm{A}=$

$\mathrm{B}=\mathrm{CO}_{2}, \mathrm{~S}=\mathrm{P}(\mathrm{OMe})_{3}$
(b) $\mathrm{A}=$

$\mathrm{B}=\mathrm{O}=\mathrm{C}=\mathrm{S}, \mathrm{O}=\mathrm{P}(\mathrm{OMe})_{3}$
(c) $\mathrm{A}=$
 $\mathrm{B}=\mathrm{CO}_{2}, \mathrm{~S}=\mathrm{P}(\mathrm{OMe})_{3}$
(d) $\mathrm{A}=$

$\mathrm{B}=\mathrm{O}=\mathrm{C}=\mathrm{S}, \mathrm{O}=\mathrm{P}(\mathrm{OMe})_{3}$
104. In trans 1, 2-dichloroethylene, the IR inactive mode is
(a) $\mathrm{C}-\mathrm{Cl}$ symmetric stretch
(b) $\mathrm{C}-\mathrm{Cl}$ asymmetric stretch
(c) $\mathrm{C}-\mathrm{H}$ asymmetric stretch
(d) In phase out of plane $\mathrm{C}-\mathrm{Cl}$ bend
105. The electrolyte solution that has the smallest Debye-length at 298 K is
(a) 0.01 M NaCl
(b) $0.01 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$
(c) $0.01 \mathrm{M} \mathrm{CuCl}_{2}$
(d) $0.01 \mathrm{M} \mathrm{LaCl}_{3}$
106. The correct statement about base hydrolysis of $\left[\mathrm{Co}(\mathrm{py})_{4} \mathrm{Cl}_{2}\right]^{+}(\mathrm{py}=$ pyridine $)$ is
(a) rate expression is, Rate $=\mathrm{k}\left[\mathrm{Co}(\mathrm{py})_{4} \mathrm{Cl}_{2}\right]^{+}\left[\mathrm{OH}^{-}\right]$
(b) reaction does not depend on hydroxide ion concentration
(c) reaction proceeds through $\mathrm{S}_{\mathrm{N}^{1}} \mathrm{CB}$ mechanism
(d) intermediate involved in this reaction is $\left[\mathrm{Co}(\mathrm{py})_{4} \mathrm{Cl}_{2}(\mathrm{OH})\right]$
107. The reaction that gives (E)-2-methylhex-3-ene as the major product is
(a)

(b)

(c)

(d)


108. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

109. The major product formed in the following reaction is

110. Match Column-I, II and III

## Column-I (metal) Column-II (enzyme)

(A) Ni
(B) Zn
(C) Mo
(I) Carbonic anhydrase
(II) Xanthine oxidase
(III) Coenzyme $\mathrm{F}_{430}$

Column-III (end product)
(X) uric acid
(Y) methane
(Z) carbonic acid

The correct match is
(a) A-III-Y, B-I-Z, C-II-X
(b) A-III-Y, B-II-X, C-I-Z
(c) A-II-X, B-I-Y, C-III-Z
(d) A-I-X, B-III-Z, C-II-Y
111. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

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

(a) $(\mathrm{A})=$

(b) $(\mathrm{A})=$

$(B)=$

(c) $(\mathrm{A})=$

(d) $(\mathrm{A})=$

$(\mathrm{B})=$

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

(a) $(\mathrm{A})=$
$(B)=$
(b) $(\mathrm{A})=$

(B) $=$

(c) $(\mathrm{A})=$

(d) $(\mathrm{A})=$

$(B)=H$

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

(a)


(b) $\mathrm{A}=\mathrm{Me}$ -

(c)

$B=$

(d)


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) $\left[\mathrm{PtCl}_{4}\right]^{2-}$
(B) $\left[\mathrm{TeCl}_{6}\right]^{2-}$
(C) $\mathrm{PF}_{3}$ and $\mathrm{SF}_{6}$
(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 $\mathrm{m} / \mathrm{z} 121,105,77,44$ is
(a)

(b)

(c)

(d)

119. The correct order of metal-carbon distance is
(a) $\mathrm{Fe}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\mathrm{Co}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\mathrm{Ni}\left(\eta^{5}-\mathrm{Cp}\right)_{2}$
(b) $\operatorname{Fe}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\mathrm{Ni}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\operatorname{Co}\left(\eta^{5}-\mathrm{Cp}\right)_{2}$
(c) $\mathrm{Ni}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\mathrm{Fe}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\mathrm{Co}\left(\eta^{5}-\mathrm{Cp}\right)_{2}$
(d) $\mathrm{Ni}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\mathrm{Co}\left(\eta^{5}-\mathrm{Cp}\right)_{2}>\mathrm{Fe}\left(\eta^{5}-\mathrm{Cp}\right)_{2}$
120. The rate constant of a second order reaction $2 \mathrm{~A} \rightarrow \mathrm{Z}$ 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 $k_{2} a_{0}$ is
(a) $\ln \left(\frac{x}{a_{0}-x}\right)$
(b) $\frac{x}{a_{0}\left(a_{0}-x\right)}$
(c) $\frac{x}{a_{0}-x}$
(d) $\ln \left(\frac{x}{a_{0}\left(a_{0}-x\right)}\right)$

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