## PAPER : CSIR-UGC-NET/JRF JUNE 2019 <br> CHEMICAL SCIENCES BOOKLET-[A]

## PART-B

21. The role of $\mathrm{H}_{3} \mathrm{PO}_{4}$ in the estimation of Fe (II) with $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ using diphenylamine sulphonate as indicator is to
(a) avoid aerial oxidation of Fe (II)
(b) reduce the electrode potential of $\mathrm{Fe}^{3+} \rightarrow \mathrm{Fe}^{2+}$
(c) stabilize the indicator
(d) stabilize $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$
22. $\mathrm{O}_{2}^{-}$is
(a) having a shorter $\mathrm{O}-\mathrm{O}$ bond length than that in $\mathrm{O}_{2}$
(b) a stronger oxidising agent than $\mathrm{O}_{2}$
(c) IR active
(d) unable to abstract proton from weak acids
23. In neutron activation analysis the radiation commonly detected is
(a) $\alpha$-rays
(b) $\beta$-rays
(c) $\gamma$-rays
(d) X-rays
24. The metal transferred by bacteria and fungi using siderophores/siderochromes is
(a) Mo
(b) Cu
(c) Fe
(d) Zn
25. Self-exchange electron transfer is fastest in
(a) $\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+/ 3+}$
(b) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+/ 3+}$
(c) $\left[\mathrm{Cr}\left(\mathrm{OH}_{2}\right)_{6}\right]^{2+/ 3+}$
(d) $\left[\mathrm{Fe}\left(\mathrm{OH}_{2}\right)_{6}\right]^{2+/ 3+}$
26. The number of $\mathrm{Ni}-\mathrm{Ni}$ bonds in $\left[\mathrm{CpNi}\left(\mu-\mathrm{PPh}_{2}\right)\right]_{2}$ complex obeying the 18 electron rule is
(a) 0
(b) 1
(c) 2
(d) 3
27. For the reaction of trans- $\left[\operatorname{IrX}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2}\right](\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{Br}, \mathrm{I})$ with $\mathrm{O}_{2}$, correct order of variation of rate with X is
(a) $\mathrm{Br}>$ I $>\mathrm{F}>\mathrm{Cl}$
(b) $\mathrm{F}>\mathrm{Cl}>\mathrm{Br}>$ I
(c) $\mathrm{F} \approx \mathrm{Cl} \approx \mathrm{Br} \approx \mathrm{I}$
(d) $\mathrm{I}>\mathrm{Br}>\mathrm{Cl}>\mathrm{F}$
28. The species that results by replacing one quarter of $\mathrm{Si}(\mathrm{IV})$ in pyrophyllite $\left[\mathrm{Al}_{2}(\mathrm{OH})_{2} \mathrm{Si}_{4} \mathrm{O}_{10}\right]$ with $\mathrm{Al}(\mathrm{III})$ [charge balance by $\mathrm{K}(\mathrm{I})$ ] is
(a) muscovite
(b) phlogopite
(c) montmorillonite
(d) talc
29. The reaction of $\mathrm{IO}_{3}^{-}$with $\mathrm{I}^{-}$in aqueous acidic medium results in
(a) $\mathrm{I}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$
(b) $\mathrm{I}_{2}$ and $\mathrm{H}_{2} \mathrm{O}_{2}$
(c) $\mathrm{IO}^{-}$and $\mathrm{H}_{2} \mathrm{O}$
(d) $\mathrm{IO}^{-}$and $\mathrm{H}_{2} \mathrm{O}_{2}$
30. The organic species isolobal to $\left[\mathrm{Fe}(\mathrm{CO})_{2}\left(\mathrm{PPh}_{3}\right)\right]^{-}$is
(a) $\mathrm{CH}_{2}^{+}$
(b) $\mathrm{CH}^{-}$
(c) $\mathrm{CH}_{3}$
(d) CH
31. The oxidation state of sulphur in the dithionous and dithionic acids, respectively, are
(a) $+4,+6$
(b) $+4,+5$
(c) $+3,+5$
(d) $+3,+6$
32. Consider the following reaction:

$$
\mathrm{Hg}^{2+}(\mathrm{aq})+\mathrm{X}^{-}(\mathrm{aq})=[\mathrm{HgX}]^{+}(\mathrm{aq})
$$

The stability constants for $[\mathrm{HgX}]^{+}(\mathrm{aq})$ for $\mathrm{X}=\mathrm{F}, \mathrm{Cl}$ and Br follow the order
(a) $\mathrm{F}<\mathrm{Cl}<\mathrm{Br}$
(b) $\mathrm{Br}<\mathrm{Cl}<\mathrm{F}$
(c) $\mathrm{Cl}<\mathrm{Br}<\mathrm{F}$
(d) $\mathrm{Br}<\mathrm{F}<\mathrm{Cl}$
33. The coordination number of Gd in $\mathrm{GdCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ is
(a) 3
(b) 6
(c) 8
(d) 9
34. Among the following, the correct statement about $\pi$-molecular orbitals $(\pi-\mathrm{MOs})$ of benzene is
(a) Only the lowest energy MO is doubly degenerate
(b) Only LUMO is doubly degenerate
(c) Only HOMO is doubly degenerate
(d) Both the HOMO nad LUMO are doubly degenerate.
35. The major product(s) formed in the following reaction is(are)

36. The number of ${ }^{1} \mathrm{H}$ NMR signals observed for the following compound is

(a) 3
(b) 4
(c) 5
(d) 6
37. The correct order of reactivity of the following dienes towards reaction with maleic anhydride is
(a) E-1-chlorobuta-1, 3-diene $<E$-penta-1, 3-diene $<E$-1-methoxybuta-1, 3-diene
(b) $E$-penta-1, 3-diene $<E$-1-chlorobuta-1, 3-diene $<E$-1-methoxybuta-1, 3-diene
(c) $E$-1-methoxybuta-1, 3-diene $<E$-1-chlorobuta-1,3-diene $<E$-penta-1, 3-diene
(d) $E$-1-methoxybuta-1, 3-diene $<E$-penta-1, 3-diene $<E$-1-chlorobuta-1, 3-diene
38. In the following equilibrium, conformer $\mathbf{B}$ is more stable than $\mathbf{A}$ when $\mathbf{R}$ is

(a) Me
(b) F
(c) Cl
(d) OMe
39. The major product formed in the following reaction is


40. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

41. The relationship between $A$ and $B$ is

(A)

(B)
(a) Homomers (identical)
(b) Enantiomers
(c) Diastereomers
(d) Conformers
42. The most stable conformation of the following molecule is

(a)

(b)

(c)

(d)

43. Reaction of deoxymonosaccharide $\mathbf{A}$ with 2 equivalents of $\mathrm{HIO}_{4}$ affords propanedial, formic acid and formaldehyde. The structure of $\mathbf{A}$ is
(a)

(b)

(c)

(d)

44. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

45. The compound that will show a base peak at $\mathrm{m} / \mathrm{z} 120$ in its E 1 mass spectrum is
(a)

(b)

(c)

(d)

46. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

47. The mobility of a divalent cation in water is $8 \times 10^{-8} \mathrm{~m}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$. The effective radius of the ion is (viscosity of water $=1 \mathrm{cP} ; \mathrm{e}=1.6 \times 10^{-19} \mathrm{C}$ )
(a) 106 pm
(b) 212 pm
(c) 424 pm
(d) 318 pm
48. The electrical double layer model among the following that consists of both fixed and diffuse layers is
(a) Helmoltz
(b) Gouy
(c) Stern
(d) Debye-Huckel
49. The lowest energy unnormalized wave function of $\mathrm{H}_{2}^{+}$molecule is ( $r_{1}$ and $r_{2}$ are the distances between the electron and nuclei 1 and 2 , respectively)
(a) $\psi=\left(e^{-r_{1} / a_{0}}+e^{-r_{2} / a_{0}}\right)$
(b) $\psi=\left(e^{-r_{1} / a_{0}}-e^{-r_{2} / a_{0}}\right)$
(c) $\psi=e^{-r_{1} / a_{0}}$
(d) $\psi=e^{-r_{2} / a_{0}}$
50. Nearest neighbour distance in a crystal system of side length $a$ is $\frac{a}{\sqrt{2}}$ in
(a) Face-centered cube
(b) Body-centered cube
(c) Trigonal primitive
(d) Primitive cube
51. For a particle of mass $m$ in a one-dimensional box of length $2 \boldsymbol{L}$, the energy of the level corresponding to $n=8$ is
(a) $\frac{h^{2}}{8 m L^{2}}$
(b) $\frac{h^{2}}{32 m L^{2}}$
(c) $\frac{4 h^{2}}{m L^{2}}$
(d) $\frac{2 h^{2}}{m L^{2}}$
52. The correct statement about HCl and DCl , among the following, is
(a) DCl has a smaller zero-point energy than HCl
(b) HCl has a smaller vibration frequency than DCl
(c) The force constant $k$ of the HCl bond is half that of DCl
(d) The reduced mass of DCl is smaller than that of HCl
53. One mole of a mono-atomic ideal gas is transformed from 300 K and 2 atm to 600 K and 4 atm . The entropy change for this process is
(a) $\frac{3}{2} R \ln 2$
(b) $\frac{1}{2} R \ln 2$
(c) $\frac{7}{2} R \ln 2$
(d) $\frac{5}{2} R \ln 2$
54. The allowed transition in an atomic system is
(a) ${ }^{3} F_{4} \rightarrow{ }^{3} D_{3}$
(b) ${ }^{3} F_{4} \rightarrow{ }^{1} D_{3}$
(c) ${ }^{3} F_{4} \rightarrow{ }^{3} P_{4}$
(d) ${ }^{3} F_{4} \rightarrow{ }^{3} D_{2}$
55. The total number of symmetry elements in diborane molecule is
(a) 2
(b) 4
(c) 6
(d) 8
56. A physical observable, ' $x$ ', appears with the probability distribution $e^{(-\mid 2 x-12))}$. The average of ' $x$ ' would be
(a) 0
(b) 3
(c) 6
(d) 12
57. The rotational partition function is expected to be the smallest for the molecule, among the following
(a) $\mathrm{H}_{2}$
(b) $\mathrm{Li}_{2}$
(c) $\mathrm{N}_{2}$
(d) $\mathrm{F}_{2}$
58. If the half-life of a reaction is inversely proportional to the square of the concentration of the reactant, the order of the reaction is
(a) 0
(b) 1
(c) 2
(d) 3
59. The degree of polymerisation $(\langle N\rangle)$ and the fraction of monomer consumed $(P)$ for a polymerization reaction are related as
(a) $\langle N\rangle=\frac{1}{1-P}$
(b) $\langle N\rangle=\frac{1}{1+P}$
(c) $\langle N\rangle=\frac{1}{P}$
(d) $\langle N\rangle=\frac{1}{P^{2}}$
60. The correct match for the compounds in Column-I with the property in Column-II is

## Column-I

(P) Dichlorodifluoromethane
(Q) Sulfadiazine
(R) Cortisone
(S) Hexachlorobenzene
(a) P-II, Q-I, R-IV, S-III
(c) P-I, Q-III, R-II, S-IV

## Column-II

(I) Anti-inflammatory
(II) Insecticidal
(III) Antibacterial
(IV) Ozone layer depletion
(b) P-IV, Q-I, R-II, S-III
(d) P-IV, Q-III, R-I, S-II

## PART - C

61. The correct statements about $\left[\mathrm{Ru}_{6} \mathrm{C}(\mathrm{CO})_{17}\right]$ cluster from the following
(1) it is an 86 electron cluster
(2) it is a closo structure type
(3) its shape is capped square pyramid
(4) carbon interacts with all the Ru centres in the cluster are
(a) 1, 2, 3 and 4
(b) 1 and 2 only
(c) 1, 2 and 3
(d) 1, 2 and 4
62. A plausible structure of the intermediate involved in the following reaction

(a)

(b)

(c)

(d)

63. In the synthesis of polydimethylsiloxane, the chain forming, branching and terminating agents respectively, are
(a) $\mathrm{Me}_{2} \mathrm{SiCl}_{2}, \mathrm{Me}_{3} \mathrm{SiCl}$ and $\mathrm{MeSiCl}_{3}$
(b) $\mathrm{Me}_{2} \mathrm{SiCl}_{2}, \mathrm{MeSiCl}_{3}$ and $\mathrm{Me}_{3} \mathrm{SiCl}$
(c) $\mathrm{MeSiCl}_{3}, \mathrm{Me}_{2} \mathrm{SiCl}_{2}$ and $\mathrm{Me}_{3} \mathrm{SiCl}$
(d) $\mathrm{Me}_{2} \mathrm{SiCl}_{2}, \mathrm{MeSiCl}_{3}$ and $\mathrm{Me}_{4} \mathrm{Si}$
64. The set among the following in which all numbers are magic numbers of nucleons is
(a) 20, 28, 50 and 126
(b) 24, 28, 82 and 126
(c) 20, 50, 80 and 184
(d) $28,50,82$ and 180
65. Incorrect statement for amperometric titration is
(a) it is based on measurement of diffusion current.
(b) its sensitivity is always higher than those of spectrophotometric titrations
(c) it does not generally require an indicator
(d) it requires inert atmosphere $\left(\mathrm{N}_{2} / \mathrm{Ar}\right)$
66. Consider the following statements with respect to Cytochrome P-450
(A) It has histidine coordinated to iron centre
(B) It is a membrane bound metalloenzyme
(C) It has $\mathrm{Fe}(\mathrm{III})$ ion in the resting state of the enzyme

The correct statement(s) is/are
(a) A, B
(b) A, C
(c) B, C
(d) A only
67. Consider the following transformation reactions in the context of co-enzyme $B_{12}$
(A) 1, 2-Carbon shift
(B) Hydration of $\mathrm{CO}_{2}$
(C) Benzene to phenol
(D) Dimethyl sulfide to
dimethyl sulfoxide
The correct statement(s) for co-enzyme $\mathrm{B}_{12}$ is/are
(a) A, C, D
(b) A, B only
(c) B, C only
(d) A only
68. The correct statements regarding B among the following
(I) Nuclear spin of ${ }^{11} \mathrm{~B}$ is greater than that of ${ }^{10} \mathrm{~B}$
(II) The polarities of $\mathrm{B}-\mathrm{H}$ bond and $\mathrm{C}-\mathrm{H}$ bonds are opposite
(III) Cross-section of neutron absorption for ${ }^{10} \mathrm{~B}$ is much more than that of ${ }^{11} \mathrm{~B}$
(IV) B reacts with boiling aq. NaOH solution to form $\mathrm{NaB}(\mathrm{OH})_{4}$ are
(a) II and III
(b) I and II
(c) III and IV
(d) II and IV
69. Choose the correct statement(s) among the following
(I) LiF is more soluble than $\mathrm{LiClO}_{4}$ in water.
(II) The standard reduction potential $\left[\mathrm{E}^{\circ}\right]$ of Li is more negative than that of Na .
(III) The heat of hydration of $\mathrm{Li}^{+}(\mathrm{g})$ is greater than that of $\mathrm{Na}^{+}(\mathrm{g})$
(a) I and II
(b) I and III
(c) II and III
(d) III only
70. Choose the correct statement(s) among the following
(I) The dihedral angle in $\mathrm{O}_{2} \mathrm{~F}_{2}$ is $0^{\circ}$.
(II) $\mathrm{OF}_{2}$ is generally prepared by reacting fluorine gas with dilute ( $2 \%$ ) aq. NaOH solution (III) $\mathrm{O}_{2} \mathrm{~F}_{2}$ can be readily reduced by $\mathrm{H}_{2} \mathrm{~S}$.
(a) I and II only
(b) I, II and III
(c) II and III only
(d) II only
71. The correct set of information is
(a) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}: \mu_{\text {observed }}=\mu_{\text {spin }} ;\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}:$ Paramagnetic
(b) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}: \mu_{\text {observed }}>\mu_{\text {spin }} ;\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}:$ Diamagnetic
(c) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}: \mu_{\text {observed }}=\mu_{\text {spin }} ;\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}:$ Diamagnetic
(d) $\left[\mathrm{Mn}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}: \mu_{\text {observed }}>\mu_{\text {spin }} ;\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}:$ Paramagnetic
72. Consider the following statements regarding electronic spectra of high spin complexes
(A) $\mathrm{Ti}^{3+}$ complexes exhibit one sharp band.
(B) $\mathrm{Co}^{2+}$ and $\mathrm{Cr}^{3+}$ complexes exhibit two broad bands.
(C) $\mathrm{Mn}^{2+}$ complexes exhibit a series of very weak and sharp bands.
(D) $\mathrm{Ni}^{2+}$ complexes exhibit three broad bands.

The correct statements are
(a) A and C
(b) A, C and D
(c) C and D
(d) B, C and D
73. Match the appropriate geometry on the right with each of the speices on the left
(A) $\mathrm{FXeO}\left(\mathrm{OSO}_{2} \mathrm{~F}\right)$
(I) linear
(B) $\mathrm{FXeN}\left(\mathrm{SO}_{2} \mathrm{~F}\right)_{2}$
(II) pyramidal
(C) $\mathrm{XeO}_{3}$
(III) T-shaped
(D) $\mathrm{XeOF}_{2}$
(IV) bent
(a) A-I, B-İ, C-II, D-III
(b) A-I, B-I, C-II, D-IV
(c) A-IV, B-I, C-II, D-III
(d) A-I, B-IV, C-II, D-III
74. Hydrolysis of trans- $\left[\mathrm{CoLCl}(\mathrm{en})_{2}\right]^{+}\left(\mathrm{L}=\mathrm{NO}_{2}^{-}, \mathrm{NCS}^{-}, \mathrm{OH}^{-}, \mathrm{Cl}^{-}\right)$results in a product (A). The tendency to form cis-isomer of the product (A) follows the order
(a) $\mathrm{L}=\mathrm{NO}_{2}^{-}<\mathrm{NCS}^{-}<\mathrm{OH}^{-}<\mathrm{Cl}^{-}$
(b) $\mathrm{L}=\mathrm{NO}_{2}^{-}<\mathrm{Cl}^{-}<\mathrm{NCS}^{-}<\mathrm{OH}^{-}$
(c) $\mathrm{L}=\mathrm{OH}^{-}<\mathrm{Cl}^{-}<\mathrm{NO}_{2}^{-}<\mathrm{NCS}^{-}$
(d) $\mathrm{L}=\mathrm{OH}^{-}<\mathrm{NCS}^{-}<\mathrm{Cl}^{-}<\mathrm{NO}_{2}^{-}$
75. Among the following reactions, those that are feasible in liquid $\mathrm{NH}_{3}$ are
(I) $\mathrm{KNO}_{3}+\mathrm{AgCl} \rightarrow \mathrm{KCl}+\mathrm{AgNO}_{3}$
(II) $\mathrm{NH}_{4} \mathrm{Br}+\mathrm{KNH}_{2} \rightarrow \mathrm{KBr}+2 \mathrm{NH}_{3}$
(III) $\mathrm{Fe}(\mathrm{CO})_{5}+2 \mathrm{e}^{-} \rightarrow\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]^{2-}+\mathrm{CO}$
(a) I, II and III
(b) I and II only
(c) I and III only
(d) II and III only
76. The cations formed upon dissolving $\mathrm{SnF}_{4}$ and $\mathrm{AuF}_{3}$ in liquid $\mathrm{BrF}_{3}$ separately, respectively are
(a) $\mathrm{SnF}_{3}^{+}$and $\mathrm{BrF}_{2}^{+}$
(b) $\mathrm{BrF}_{2}^{+}$and $\mathrm{AuF}_{2}^{+}$
(c) $\mathrm{BrF}_{2}^{+}$only
(d) $\mathrm{SnF}_{3}^{+}$and $\mathrm{AuF}_{2}^{+}$
77. Consider the following reactions:
(A)


(C)


$+\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}_{2}$


The reaction(s) which will NOT produce ethane as a product is/are
(a) A
(b) B
(c) C
(d) A and C
78. Donor mode of NO ligand depends on the metal. Now, consider the following complexes (in gaseous state).
(A) $\left[\operatorname{IrCl}(\mathrm{CO})\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{NO})\right]^{+}$
(B) $\left[\mathrm{RuCl}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{NO})_{2}\right]^{+}$
(C) $\left[\mathrm{Co}(\mathrm{NCS})(\text { diars })_{2}(\mathrm{NO})\right]^{+}$, where diars $=o-\left(\mathrm{Me}_{2} \mathrm{As}\right)_{2} \mathrm{C}_{6} \mathrm{H}_{4}$
(D) $\left[\mathrm{Cr}(\mathrm{CN})_{5}(\mathrm{NO})\right]^{3-}$

The complex (es) that do NOT exhibit bent NO coordination mode is/are
(a) A and B
(b) C and D
(c) D only
(d) B only
79. An aqueous solution of metal ion (A) gives a blood-red colored product (B) upon reaction with KSCN. Upon dropwise addition of NaF , the complex turns to a colorless compound (C). Identify A, $B$ and $C$
(a) aq. $\mathrm{Fe}(\mathrm{II}),\left[\mathrm{Fe}(\mathrm{SCN})\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{+}$and $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
(b) aq. $\mathrm{Fe}(\mathrm{III}),\left[\mathrm{Fe}(\mathrm{SCN})\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{2+}$ and $\left[\mathrm{FeF}_{6}\right]^{3+}$
(c) aq. $\mathrm{Fe}(\mathrm{II}),\left[\mathrm{Fe}(\mathrm{SCN})\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{+}$and $\mathrm{FeF}_{3}$
(d) aq. $\mathrm{Fe}(\mathrm{III}),\left[\mathrm{Fe}(\mathrm{SCN})_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}\right]^{+}$and $\mathrm{FeF}_{3}$
80. Considering $\sigma$-bonding only, in the MO diagram of a metal complex with trigonal bipyramidal (TBP) geometry, the d-orbitals which remain non-bonding are
(a) $d_{z^{2}}$ and $d_{x z}$
(b) $d_{x z}$ and $d_{y z}$
(c) $d_{x^{2}-y^{2}}$ and $d_{x y}$
(d) $d_{z^{2}}$ and $d_{y z}$
81. The correct sequence of reactions for the preparation of $\mathbf{A}$ is

(A)
(a)


1. (i) $n-\mathrm{BuLi}$,

(b)

2. (i) $n-B u L i$,

(c)

3. (i) Mg , $\xrightarrow[\text { 2. } \mathrm{PCC}]{\text { (ii) } \mathrm{HCHO}}$

4. PC
(d)


5. (i) $n-B u L i$,

6. Structure of $\mathbf{A}$ and $\mathbf{B}$ in the following reactions are


(c) $\mathrm{A}=$


(d) $\mathrm{A}=$

7. The major product of the following reaction is

(a)

(b)

(c)

(b)

8. The compound that exhibits the following spectral data is

IR : (v) $1685 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR : $\delta 7.84(\mathrm{~d}, \mathrm{~J}=8 \mathrm{~Hz}, 2 \mathrm{H}), 7.60(\mathrm{~d}, \mathrm{~J}=8 \mathrm{~Hz}, 2 \mathrm{H}), 3.65(\mathrm{t}, \mathrm{J}=7 \mathrm{~Hz}, 2 \mathrm{H})$, $3.18(\mathrm{t}, \mathrm{J}=7 \mathrm{~Hz}, 2 \mathrm{H}), 2.25($ pentet, $\mathrm{J}=7 \mathrm{~Hz}, 2 \mathrm{H}) \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR : $\delta 28,36,45,128,130,133$, 137, 197 ppm; EI MS m / z : 200, 198(1:1), 185, $183(1: 1)$
(a)

(b)

(c)


(d)

85. The major product of the following reaction sequence is

(a)

(b)

(c)

(d)

86. The major products $(\mathbf{A})$ and $(\mathbf{B})$ of the following reaction sequence are

(a) $\mathrm{A}=$



(c) $\mathrm{A}=$


(d) $\mathrm{A}=$


87. The major product of the following reaction is

(a)

88. Structures of the products (A) and (B) in the following photo-deprotection reactions are


(a) $\mathrm{A}=$


(b) $\mathrm{A}=$


(c) $\mathrm{A}=$


(d) $\mathrm{A}=$


89. Structure of the monoterpene (A) that undergoes following degradation is
(a)

(b)

(A) $\xrightarrow[\text { then } \mathrm{CrO}_{3}]{\text { dilute } \mathrm{KMnO}_{4}}$ keto-lactone


(c)

(d)

90. The major products $(\mathbf{A})$ and $(\mathbf{B})$ in the following reaction sequence are

(a) $\mathrm{A}=$

$B=$

(b)


(c) $\mathrm{A}=$


(d) $\mathrm{A}=$


91. The major products $(\mathbf{A})$ and $(\mathbf{B})$ in the following reaction sequence are

(a) $\mathrm{A}=$


(b) $\mathrm{A}=$


(c) $\mathrm{A}=$


(d) $\mathrm{A}=$


92. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

93. The major products $(\mathbf{A})$ and $(\mathbf{B})$ in the following reactions are

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

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

(c) $\mathrm{A}=$


(d) $\mathrm{A}=$


94. The major product formed in the following reaction is
(a)

(b)

(c)

(d)

95. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

96. The major products $(\mathbf{A})$ and $(\mathbf{B})$ formed in the following reaction sequence are

(a)


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


(c)

$B=$

(d) $\mathrm{A}=$


cycloocta-1, 2-diene
97. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

98. The structure of product $(\mathbf{B})$ formed in the following reaction sequence is

(a)

(b)

(c)

(d)

99. The major products $(\mathbf{A})$ and $(\mathbf{B})$ in the following reaction sequence are

(a)


(b)


(c)
 $\mathrm{B}=\mathrm{HO}$

(d)


100. Reaction of styrene $\left(\mathrm{PhCH}=\mathrm{CH}_{2}\right)$ with HBr gives a mixture of regioisomers $\mathbf{A}$ (major) and $\mathbf{B}$ (minor). The ${ }^{1} \mathrm{H}$ NMR spectrum of the mixture shows four signals, amongst others, at $\delta 5.17,3.53,3.15$ and 2.00 ppm with relative integration of $2: 1: 1: 6$, respectively. The molar ratio of $\mathbf{A}$ and $\mathbf{B}$ is
(a) $3: 2$
(b) $4: 1$
(c) $2: 1$
(d) $3: 1$
101. The energy functional from a trial wave function is

$$
E(\alpha)=\left(\alpha^{2}-3 \alpha\right) / 6
$$

The variationally optimized energy is
(a) $-\frac{1}{2}$
(b) $-\frac{3}{8}$
(c) $\frac{3}{2}$
(d) $\frac{3}{8}$
102. A satisfactory spin wave function for an excited helium atom is
(a) $\frac{1}{\sqrt{2}}[\alpha(1) \beta(2)+\alpha(2) \beta(1)]$
(b) $\alpha(1) \beta(2)$
(c) $\frac{1}{\sqrt{2}}[\alpha(1) \alpha(2)+\beta(1) \beta(2)]$
(d) $\alpha(2) \beta(1)$
103. For a linear molecule the mean energies for translation, rotation $\left(T \gg \theta_{R}\right)$ and vibration $\left(T \gg \theta_{V}\right)$ follow ratio:
(a) $1: \frac{3}{2}: 1$
(b) $\frac{3}{2}: 1: 1$
(c) $1: \frac{1}{2}: 1$
(d) $\frac{1}{2}: 1: 1$
104. The highest energy $\pi$-molecular orbital for the allyl system is
(a) $\frac{1}{\sqrt{2}} \chi_{1}+\frac{1}{2} \chi_{2}+\frac{1}{\sqrt{2}} \chi_{3}$
(b) $\frac{1}{\sqrt{2}} \chi_{1}-\frac{1}{\sqrt{2}} \chi_{3}$
(c) $\frac{1}{2} \chi_{1}-\frac{1}{\sqrt{2}} \chi_{2}+\frac{1}{2} \chi_{3}$
(d) $\frac{1}{\sqrt{2}} \chi_{1}-\frac{1}{2} \chi_{2}-\frac{1}{\sqrt{2}} \chi_{3}$
105. An unnormalized wave function of the hydrogen atom is given by $r^{2} e^{-\frac{r}{3}}\left(3 \cos ^{2} \theta-1\right)$. The three quantum numbers, $n, \ell$ and $m$, associated with this orbital are, respectively.
(a) $2,2,0$
(b) 2, 1, 1
(c) $3,2,0$
(d) $3,1,1$
106. The $\pi$-orbital $p_{1}+p_{2}-p_{3}-p_{4}$ of cis-butadiene belongs to the irreducible representation

| $C_{2 v}$ | $E$ | $C_{2}$ | $\sigma_{v}$ | $\sigma_{v}^{\prime}$ |
| :---: | :---: | :---: | :---: | :---: |
| $A_{1}$ | 1 | 1 | 1 | 1 |
| $A_{2}$ | 1 | 1 | -1 | -1 |
| $B_{1}$ | 1 | -1 | 1 | -1 |
| $B_{2}$ | 1 | -1 | -1 | 1 |

(a) $A_{1}$
(b) $A_{2}$
(c) $B_{1}$
(d) $B_{2}$
107. The number of times the $A_{1}$ representation appears in the representation $\Gamma$ of the $C_{2 v}$ point group given below is

| $C_{2 v}$ | $E$ | $C_{2}$ | $\sigma_{v}$ | $\sigma_{v}^{\prime}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\Gamma$ | 3 | 1 | 1 | 3 |

(a) 1
(b) 2
(c) 3
(d) 4
108. The populations of proton spins in the highest energy level of a sample in magnetic fields of 1.5 T and 7.0 T are $N^{\prime}$ and $N$, respectively. The value of $\ln \frac{N^{\prime}}{N}$ is ( $\gamma, h, k, T$ are gyromagnetic ratio of the proton, Planck's constant, Boltzmann constant and temperature of the sample, respectively; assume that the partition functions for both systems can be approximated as 1)
(a) $5.5 \gamma \hbar / \mathrm{kT}$
(b) $\frac{3}{14} \gamma \hbar / k T$
(c) $\frac{14}{3} \gamma \hbar / k T$
(d) $8.5 \gamma \hbar / k T$
109. The difference between standard molar entropies of two mono-atomic gases (A) and (B) $\left(S_{m, A}^{0}-S_{m, B}^{0}\right)$ at a given temperature is (given that the molar mass of (A) is twice the molar mass of (B))
(a) $\frac{3}{2} R \ln 2$
(b) $R \ln 2$
(c) $\frac{5}{2} R \ln 2$
(d) $\frac{7}{2} R \ln 2$
110. A non-ideal gas follows the equation,

$$
P=\frac{R T}{V_{m}}\left[1+\frac{B}{V_{m}}\right]
$$

where B is a function of temperature only. The deviation in internal energy from that of an ideal gas, $U-U_{\text {ideal }}$, is given by
(a) $\frac{-R T}{V_{m}}\left(\frac{\partial B}{\partial T}\right)_{V}$
(b) $\frac{-R T^{2}}{V_{m}}\left(\frac{\partial B}{\partial T}\right)_{V}$
(c) $\frac{-R T^{2}}{V_{m}} B$
(d) $\frac{-R T}{V_{m}} B$
111. The gas phase decomposition of A at 1000 K follows two decomposition paths

|  | Elementary process | Rate constant |
| :---: | :---: | :---: |
| $(i)$ | $A \rightarrow B+C$ | $3 s^{-1}$ |
| $(i i)$ | $A \rightarrow P+Q$ | $5 s^{-1}$ |

The maximum theoretical percentage yield of $P$ at 1000 K is
(a) 62.5
(b) 60
(c) 166
(d) 37.5
112. Photochemistry of a molecule, M , is described as by the mechanism

|  | Elementary process | Rate |
| :---: | :---: | :---: |
| $(i)$ | $M+h v \rightarrow M^{*}$ | $I_{a b s}$ |
| $(i i)$ | $M^{*}+Q \rightarrow M+Q$ | $k_{Q}[Q]\left[M^{*}\right]$ |
| $(i i i)$ | $M^{*} \rightarrow M+h v_{F}$ | $0.2\left[M^{*}\right]$ |

The intercept at $[\mathrm{Q}]=0$ is 4 for the inverse of fluorescence intensity $\left(I / I_{F}\right)$ vs $[Q]$ plot. The value of $I_{\text {abs }}$ is
(a) 4
(b) 0.25
(c) 20
(d) 0.8
113. Above the critical micelle concentration (CMC), the option which correctly describes the variation of molar conductivity with increase in concentration of sodium dodecylsulphate in aqueous solution is
(a) molar conductivity increases sharply, but the solution does not remain colloidal
(b) molar conductivity decreases sharply, but the solution remains colloidal
(c) molar conductivity decreases sharply and dissociation into monomers also occurs sharply
(d) molar conductivity increases sharply with large loss of entropy
114. When two moles of liquid $A$ are mixed with two moles of liquid $B$ at 300 K , the excess molar Gibbs energy of the solution is $-1.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$. The corresponding value of Gibbs energy of mixing (in kJ ) is closest to ( $\mathrm{R}=8.3 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ )
(a) -12.9
(b) -6.0
(c) -1.5
(d) -0.9
115. A sample of 2.0 moles of $\mathrm{O}_{2}(\mathrm{~g})$ (assumed ideal) at 500 K is expanded from 5 L to 50 L under adiabatic and reversible conditions. The change in its internal energy (in kJ ) is close to

$$
\left(R=8.3 \mathrm{JK}^{-1} \mathrm{~mol}^{-1} ; C_{V, m}=\frac{5}{2} R\right)
$$

(a) -22.5
(b) -12.5
(c) -19.1
(d) -7.5
116. The reaction rate of a self-catalyzed polyesterification reaction is given as

$$
-\frac{d[\mathrm{COOH}]}{d t}=k[\mathrm{COOH}]^{2}[\mathrm{OH}]
$$

If $[M]_{0}$ is the initial concentration of hydroxyl and carboxyl monomers, then the degree of polymerization, $\langle N\rangle$ is given by
(a) $\langle N\rangle=2[M]_{0}^{2} k t$
(b) $\langle N\rangle^{2}=2[M]_{0}^{2} k t$
(c) $\langle N\rangle^{2}=2[M]_{0}^{2} k t+1$
(d) $\langle N\rangle^{2}=2[M]_{0} k t+1$
117. The correct relationship among the following, for a tetragonal $\left(a=b \neq c ; \alpha=\beta=\gamma=90^{\circ}\right)$ crystal system, is
(a) $\sin ^{2} \theta=\frac{\lambda^{2}}{4 a^{2}}\left[c^{2}\left(h^{2}+k^{2}\right)+a^{2} \ell^{2}\right]$
(b) $\sin ^{2} \theta=\frac{\lambda^{2}}{4 a^{2} c^{2}}\left[c^{2}\left(h^{2}+k^{2}\right)+a^{2} \ell^{2}\right]$
(c) $\sin ^{2} \theta=\frac{\lambda^{2}}{4 c^{2}}\left[a^{2}\left(h^{2}+k^{2}\right)+c^{2} \ell^{2}\right]$
(d) $\sin ^{2} \theta=\frac{\lambda^{2}}{4 a^{2}}\left[h^{2}+k^{2}+\ell^{2}\right]$
118. If the overpotential of an electrolysis process is increased from 0.5 V to 0.6 V , then the ratio of current densities $\left(\ln \frac{J_{0.6}}{J_{0.5}}\right)$ of the electrolysis will be equal to (given transfer co-efficient $=0.5$ )
(a) $0.5 \frac{F}{R T}$
(b) $0.05 \frac{F}{R T}$
(c) $0.1 \frac{F}{R T}$
(d) $0.01 \frac{F}{R T}$
119. The chemical potential $(\mu)$ of a 2 molar $\mathrm{Na}_{2} \mathrm{SO}_{4}$ solution is expressed in terms of mean ionic activity co-efficient $\left(\gamma_{ \pm}\right)$as
(a) $\mu^{0}+5 R T \ln 2+3 R T \ln \gamma_{ \pm}$
(b) $\mu^{0}+3 R T \ln 2+3 R T \ln \gamma_{ \pm}$
(c) $\mu^{0}+3 R T \ln \gamma_{ \pm}$
(d) $\mu^{0}+4 R T \ln \gamma_{ \pm}$
120. The Birge-Sponer plot between $\Delta G_{v+\frac{1}{2}}=\left(\varepsilon_{v+1}-\varepsilon_{v}\right)$ and $(v+1)$ for CO is a straight line with slope of $-14 \mathrm{~cm}^{-1}$ and intercept of $2170 \mathrm{~cm}^{-1}$. The approximate value of dissociation energy of CO (in $\mathrm{cm}^{-1}$ )is (Assume CO as an anharmonic oscillater with the energy expression)

$$
\left.\varepsilon_{v}=\left(v+\frac{1}{2}\right) \omega-\left(v+\frac{1}{2}\right)^{2} x_{e} \omega ; D=\frac{\omega}{4 x_{e}}\right)
$$

(a) 42044
(b) 84088
(c) 168175
(d) 336350

