## ENTRANCE EXAMINATIONS - 2023

## Ph.D. Chemistry

TIME: 2 HOURS
MAXIMUM MARKS: 70
HALL TICKET NUMBER:


1. Write your HALL TICKET NUMBER in the space provided above and also on the OMR ANSWER SHEET given to you.
2. Make sure that pages numbered from 1-23 are present (excluding 5 pages assigned for rough work).
3. There are eighty (80) multiple-choice questions in this paper (20 in Part-A and $\mathbf{6 0}$ in Part-B). You are required to answer all questions of Part-A and a maximum of 20 questions of Part-B. If more than the required number of questions are answered in Part-B, only the first $\mathbf{2 0}$ questions will be evaluated.
4. Each question in Part-A and Part-B carries $\mathbf{1 . 7 5}$ marks.
5. There is no negative marking for both Part-A and Part-B.
6. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
7. Handover the OMR answer sheet to the invigilator at the end of the examination.
8. In case of a tie, the marks obtained in the first 20 questions (Part-A) will be used to determine the order of merit.
9. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
10. Calculators are allowed. Cell phones are not allowed.
11. Useful constants are provided just above Part-A in the question paper.
12. OMR without hall ticket number will not be evaluated and University shall not be held responsible.

## Useful Constants:

Rydberg constant $=109737 \mathrm{~cm}^{-1}$; Faraday constant $=96500 \mathrm{C}$; Planck constant $=6.625 \times 10^{-34} \mathrm{~J} \mathrm{~s}$; Speed of light $=2.998 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1} ;$ Boltzmann constant $=1.380 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1} ;$ Gas constant $=8.314$ $\mathrm{J} \mathrm{K}^{-1} \mathrm{~mol}^{-1}=0.082 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}=1.987 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$; Mass of electron $=9.109 \times 10^{-31} \mathrm{~kg}$; Mass of proton $=1.672 \times 10^{-27} \mathrm{~kg}$; Charge of electron $=1.6 \times 10^{-19} \mathrm{C} ; 1 \mathrm{bar}=10^{5} \mathrm{~N} \mathrm{~m}^{-2} ; \mathrm{RT} / \mathrm{F}$ (at $298.15 \mathrm{~K})=0.0257 \mathrm{~V}$; Avogadro number $=6.022 \times 10^{23} ; 1 \mathrm{amu}=1.66 \times 10^{-27} \mathrm{~kg}$

## PART-A

1. For a first order reaction with stoichiometric equation, $2 \mathrm{~A} \rightarrow$ Products, the concentration of A at time $t,[\mathrm{~A}]$, is related to initial concentration, $[\mathrm{A}]_{0}$, as
[A] $\ln [A]_{0}=2 \ln [A]+k t$
[B] $\ln [A]_{0}=\ln [A]+k t$
[C] $\ln [A]_{0}=\ln [A]+2 k t$
[D] $\ln [A]_{0}=2 \ln [A]+2 k t$
2. With increasing temperature, the electrical conductivity of metals and semiconductors
[A] decrease and increase, respectively
[B] increase and decrease, respectively
[C] increase in both cases
[D] decrease in both cases
3. Suppose adsorption of ozone on a particular surface takes place with dissociation into $\mathrm{O}+$ $\mathrm{O}_{2}$. If the adsorption follows Langmuir type isotherm, then the pressure dependence of the fractional coverage $(\theta)$ is:
[A] $\frac{K p}{1+K p}$
[B] $\frac{K p^{1 / 3}}{1+K p^{1 / 3}}$
[C]

$$
\frac{(K p)^{1 / 2}}{1+(K p)^{1 / 2}}
$$

[D] $\frac{K p^{1 / 4}}{1+K p^{1 / 4}}$
4. The correct expression of chemical potential as a function of molecular partition function is ( $q$ : partition function of a molecule, $T$ : temperature, $k_{B}$ : Boltzmann constant, $N$ : number of molecules)
[A] $\mu=k_{B} T \ln (q / N)$
[B] $\mu=-k_{B} T \ln (q / N)$
[C] $\mu=-k_{B} T(N / q)$
[D] $\mu=k_{B} T(N / q)$
5. The contribution of an unshifted atom to the total character in the matrix representation of the symmetry operation $C_{4}$ is
[A]
-1
[B]
0
[C]
1
[D]
2
6. The enthalpy change of a chemical reaction is zero. At a given temperature, the chemical equilibrium will be shifted towards reactant side ( $K<1$ ), if
[A] the energy levels are equally dense both for the reactants and products
[B] the energy levels of the reactants are denser than the products
[C] the energy levels of the products are denser than the reactants
[D] equilibrium constant is independent of the energy levels of reactants and products
7. Eigen value of an anti-Hermitian operator is
[A] zero
[B] real positive
[C] real negative
[D] imaginary
8. The carbonyl absorption bands in the IR spectra of two compounds, X and Y are observed at

x


Y
[A] (X) $1695 \mathrm{~cm}^{-1}$ and (Y) $1725 \mathrm{~cm}^{-1}$
[B] (X) $1725 \mathrm{~cm}^{-1}$ and (Y) $1695 \mathrm{~cm}^{-1}$
[C] (X) $1615 \mathrm{~cm}^{-1}$ and (Y) $1715 \mathrm{~cm}^{-1}$
[D] (X) $1715 \mathrm{~cm}^{-1}$ and (Y) $1615 \mathrm{~cm}^{-1}$
9. The most suitable condition for the following transformation is

[A] $\mathrm{H}_{2} \mathrm{O}_{2} / \mathrm{I}_{2} / \mathrm{H}_{2} \mathrm{O}$
[B] $\mathrm{H}_{2} \mathrm{O}_{2} / \mathrm{Cl}_{2} / \mathrm{H}_{2} \mathrm{O}$
[C] $\mathrm{H}_{2} \mathrm{O}_{2} / \mathrm{F}_{2} / \mathrm{H}_{2} \mathrm{O}$
[D] $\mathrm{H}_{2} \mathrm{O}_{2} / \mathrm{Br}_{2} / \mathrm{H}_{2} \mathrm{O}$
10. The most suitable reagent for reaction given below is

[A] DDQ
[B] PCC
[C] MMPPA
[D] $m$-CPBA
11. The appropriate condition to obtain (Z)-but-2-ene from 2-butyne is
[A] $5 \% \mathrm{Pd} / \mathrm{C}, \mathrm{H}_{2}$
[B] $\mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}, \mathrm{H}_{2}$
[C] $5 \% \mathrm{Pd} / \mathrm{CaCO}_{3}$, lead salts, $\mathrm{H}_{2}$
[D] Na, liq- $\mathrm{NH}_{3}$
12. The compound having a highest barrier for rotation about the marked bond is
[A]

[B]

[C]

[D]

13. Stable ions I \& II formed in the following reactions are:


[A]

[B]

[C]

\&

[D]


14. Which of the following is a non-reducing sugar?
[A] Maltose
[B] Lactose
[C] Trehalose
[D] Cellobiose
15. Siderophores display strong affinity for
[A] $\mathrm{Fe}^{2+}$
[B] $\mathrm{Fe}^{3+}$
[C] $\mathrm{Mn}^{3+}$
[D] $\mathrm{Mn}^{2+}$
16. The possible coordination modes of an alkyne ligand with metal centre(s) is
[A] 1, 2 and 4
[B] 1, 2 and 3
[C] 1, 2, 3 and 4
[D] 1 and 2
17. Which one of the following statements is not correct?
[A] Brønsted-Lowry acids are also Arrhenius acids.
[B] Brønsted-Lowry bases are not Arrhenius bases.
[C] Brønsted-Lowry acids are also Lewis acids.
[D] Bransted-Lowry bases are also Lewis bases.
18. The active sites of dioxygen carriers, hemocyanin and hemerythrin contain
[A] Cu and Cu respectively.
[B] Co and Fe , respectively.
[C] Fe and Fe respectively.
[D] Cu and Fe , respectively.
19. If the drinking water is to maintain 2.0 ppm of KI , the number of liters of water that can be iodinated with 500 g of KI is
[A] 1000 liters.
[B] $5.2 \times 10^{3}$ liters.
[C] $\quad 10.0 \times 10^{5}$ liters.
[D] $2.5 \times 10^{5}$ liters.
20. Which one of the octahedral configurations will have spin only contribution for its magnetic moment
[A] $d^{5}$ (high spin)
[B] $d^{7}$ (high spin)
[C] d ${ }^{4}$ (low spin)
[D] $\mathrm{d}^{5}$ (low spin)

$$
C-10
$$

## PART-B

21. If the Debye temperatures of two insulating solids are in the ratio 2.0:3.0, the ratio of their heat capacities at the same temperature (in the low temperature range) will be
[A] 2.0:3.0
[B] 3.4:1.0
[C] 3.0:2.0
[D] 0.4:1.0
22. In a cubic crystal system, ratio of the spacing of the Miller planes, (110) and (251), $\frac{d_{110}}{d_{251}}$ is
[A] 15.0
[B] 5.48
[C] 3.87
[D] 0.26
23. The majority charge carriers in the extrinsic semiconductors, As-doped Ge and In-doped Ge are, respectively,
[A] electrons and holes
[B] holes and electrons
[C] excitons and holes
[D] electrons and excitons
24. Critical micelle concentration (CMC) of surfactant is determined by measuring various physical properties as a function of surfactant concentration as shown in the figure below. Plots (A), (B) and (C) in the figure represent:

[A] surface tension, osmotic pressure and molar conductivity, respectively
[B] molar conductivity, osmotic pressure and surface tension, respectively
[C] molar conductivity, surface tension and osmotic pressure, respectively
[D] osmotic pressure, molar conductivity and surface tension, respectively
25. The equation of state of a certain gas is given by $=\frac{R T}{V}+\frac{a+b T}{V^{2}}$, where $a$ and $b$ are constants. The $\left(\frac{\partial V}{\partial T}\right)_{p}$ of this gas is:
[A] $\frac{R V+b}{2 p V+R T}$
[B] $\frac{R V+b}{2 p V-R T}$
[C] $\frac{V+R b}{2 p V-R T}$
[D] $\frac{R V+b}{2 R V-p T}$
26. In a certain NMR spectrometer, ${ }^{1} \mathrm{H}$ absorbs at 42.577 MHz . The magnetic field (in T ) at which the spectrometer operates is nearly equal to (Gyromagnetic ratio of ${ }^{1} \mathrm{H}$ is $267.520 \times 10^{6} \mathrm{rad} \mathrm{T}^{-1} \mathrm{~s}^{-1}$ )
[A] 6.5
[B] 5.0
[C] 2.5
[D] 1.0
27. For a set of two parallel first order reactions, $\mathrm{A} \rightarrow \mathrm{P}$ and $\mathrm{A} \rightarrow \mathrm{Q}$ with rate constants, $k_{1}$ and $k_{2}$, respectively, the concentration of P at any time $t$ is expressed as $\left([\mathrm{A}]_{0}\right.$ : initial concentration of A):
[A] $\frac{k_{1}[\mathrm{~A}]_{0}}{k_{1}+k_{2}}\left(1-e^{-k_{1} t}\right)$
[B] $\frac{k_{1}[\mathrm{~A}]_{0}}{k_{2}}\left(1-e^{-k_{1} t}\right)$
[C] $\frac{k_{1}[\mathrm{~A}]_{0}}{k_{1}+k_{2}}\left(1-e^{-\left(k_{1}+k_{2}\right) t}\right)$
[D] $\frac{k_{1}[\mathrm{~A}]_{0}}{k_{2}}\left(1-e^{-\left(k_{1}+k_{2}\right) t}\right)$
28. For a two-level system having energies $k_{B} T$ and $2 k_{B} T$, the occupation probability of energy levels is given by the Boltzmann distribution. If the upper energy level is doubly degenerate, the value of the partition function is nearly equal to
[A] 0.503
[B] 0.639
[C] 0.871
[D] 1.104
29. The oxygen molecule has a vibrational wavenumber of $1580 \mathrm{~cm}^{-1}$. Its vibrational temperature $\left(\theta_{v}\right)$ is nearly equal to (in K )
[A] 569
[B] 1138
[C] 2276
[D] 3414
30. A molecule belongs to the $\mathrm{C}_{2 \mathrm{~h}}$ point group. The character table for the $\mathrm{C}_{2 \mathrm{~h}}$ point group is given below. Which transition among the following is allowed by a $x$-polarized light in infrared spectroscopy?

| $\dot{C}_{2 h}$ | $\hat{E}$ | $\hat{C}_{2}$ | $\hat{i}$ | $\hat{\sigma}_{h}$ |  |
| :--- | :--- | ---: | ---: | ---: | :--- |
| $A_{g}$ | 1 | 1 | 1 | 1 | $R_{z}$ |
| $B_{g}$ | 1 | -1 | 1 | -1 | $R_{x} ; R_{y}$ |
| $A_{u}$ | 1 | 1 | -1 | -1 | $z$ |
| $B_{u}$ | 1 | -1 | -1 | 1 | $x ; y$ |

[A]
$a_{u} \rightarrow a_{u}$
[C]
$b_{g} \rightarrow a_{g}$
[B]
$a_{u} \rightarrow b_{g}$
[D]
$b_{u} \rightarrow b_{g}$
31. The mean ionic activity coefficient $\left(\gamma_{ \pm}\right)$of 0.005 M aqueous solution of $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$ at 25 ${ }^{\circ} \mathrm{C}$ is nearly equal to (assume complete dissociation)
[A] 0.01
[B] 0.35
[C] 0.60
[D] 0.75
32. 5 moles of an ideal monatomic gas undergo reversible adiabatic expansion from $4 \mathrm{dm}^{3}$ to $16 \mathrm{dm}^{3}$ at 300 K . The change in internal energy (in kJ ) is nearly equal to
[A] 0
[B] -11
[C] -22
[D] -44
33. Koopmann's theorem states, within Hartree-Fock limit (with IE, EA, $\varepsilon_{a}$ and $\varepsilon_{r}$ representing ionization energy, electron affinity, energy of occupied orbital and energy of virtual orbital, respectively)
[A] $\mathrm{IE}=-\varepsilon_{\mathrm{a}}$ and $\mathrm{EA}=-\varepsilon_{\mathrm{r}}$
[B] $\mathrm{IE}=\varepsilon_{\mathrm{a}}$ and $\mathrm{EA}=\varepsilon_{\mathrm{r}}$
[C] IE $=-\varepsilon_{\mathrm{r}}$ and $E A=-\varepsilon_{a}$
[D] $\mathrm{IE}=\varepsilon_{\mathrm{r}}$ and $\mathrm{EA}=\varepsilon_{\mathrm{a}}$
34. If two operators commute with each other, which of the following are true?
i. their eigenvalues are simultaneously measurable without uncertainty
ii. their eigenvalues are simultaneously measurable with uncertainty
iii. they will have common complete set of eigenfunctions
iv. they cannot have common complete set of eigenfunctions
[A] (i) and (iv)
[B] (i) and (iii)
[C] (ii) and (iv)
[D] (ii) and (iii)
35. The spatial part of the valence bond wave function of $\mathrm{H}_{2}$ molecule is given by $\psi=N\left[1 s_{a}(1) 1 s_{b}(2)-1 s_{a}(2) 1 s_{b}(1)\right] . a$ and $b$ are the two H nuclei and 1 and 2 represent two electrons. $N$ is the normalization constant. The electronic term symbol corresponding to the above wave function is
[A] ${ }^{1} \Sigma$
[B] ${ }^{3} \Sigma$
[C] ${ }^{1} \Pi$
[D] ${ }^{3} \Pi$
36. At 298 K , the standard free energy change $\left(\Delta \mathrm{G}^{0}\right)$ in $\mathrm{kJ} / \mathrm{mol}$ for the cell reaction $\mathrm{Cu}^{2+}(a q)+$ $\mathrm{Zn}(s) \rightarrow \mathrm{Cu}(s)+\mathrm{Zn}^{2+}(a q)$ is $\left(E_{C u^{2+} / C u}^{0}=0.34 \mathrm{~V}\right.$ and $\left.E_{Z n^{2+} / Z n}^{0}=-0.76 \mathrm{~V}\right)$
[A] +106
[B] +212
[C] -106
[D] -212
37. The spacing between lines in the pure rotational spectrum of ${ }^{11} \mathrm{~B}^{2} \mathrm{D}$ is $13.07 \mathrm{~cm}^{-1}$. The bond length (in pm ) of the molecule is nearly equal to
[A] 123
[B] 213
[C] 232
[D] 312
38. In rotational Raman spectroscopy, the change in the rotational quantum number for the Stokes and anti-Stokes lines, respectively, are
[A] $\Delta J=+1$ and $\Delta J=-1$
[B] $\Delta J=-1$ and $\Delta J=+1$
[C] $\Delta J=-2$ and $\Delta J=+2$
[D] $\Delta J=+2$ and $\Delta J=-2$
39. The most populated rotational level of $\mathrm{Cl}_{2}\left(\mathrm{~B}=0.244 \mathrm{~cm}^{-1}\right)$ at $25^{\circ} \mathrm{C}$ is
[A] $J=5$
[B] $J=10$
[C] $J=15$
[D] $J=20$
40. The correct relationship for a free particle-in-a-box of length $a$ is
[A] $\frac{\langle E\rangle}{\langle p\rangle}=\frac{h^{2}}{2 m}$
[B] $\frac{\langle E\rangle}{\langle p\rangle}=\frac{1}{2 m}$
[C] $\frac{\langle E\rangle}{\left\langle p^{2}\right\rangle}=\frac{h^{2}}{2 m}$
[D] $\frac{\langle E\rangle}{\left\langle p^{2}\right\rangle}=\frac{1}{2 m}$
41. Predict the major product in the following transformation.

[A]

[B]

[C]

[D]

42. Predict the major product in the following transformation.

[A]

[B]

[C]

[D]


$$
c-10
$$

43. Identify $\mathbf{X}$ and $\mathbf{Y}$ in the following reaction sequence:

[A]

[B]

[C]

[D]

44. Identify $\mathbf{X}$ and $\mathbf{Y}$ in the following reaction sequence:

[A]

[B]

[C]

[D]
 $Y=$

45. Predict the major product in the following transformation.

[A]

[B]

[C]

[D]

46. The major enantiomer formed in the below reaction is:

[A]

[B]

[C]

[D]

47. The ${ }^{1} \mathrm{H}$-NMR spectrum of a compound with molecular formula $\mathrm{C}_{5} \mathrm{H}_{6} \mathrm{O}_{2}$ is given below. Its IR spectrum gives an intense peak at $\sim 1735 \mathrm{~cm}^{-1}$ and medium-intensity sharp peaks at 3270 and $2118 \mathrm{~cm}^{-1}$. The compound is:

[A] $\mathrm{H}-\mathrm{C} \equiv \mathrm{C}-\mathrm{CH}_{2}-(\mathrm{C}=\mathrm{O})-\mathrm{O}-\mathrm{CH}_{3}$
[B] $\mathrm{CH}_{3}-\mathrm{CH}_{2}-(\mathrm{C}=\mathrm{O})-\mathrm{O}-\mathrm{C} \equiv \mathrm{C}-\mathrm{H}$
[C] $\mathrm{CH}_{3}-(\mathrm{C}=\mathrm{O})-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{C} \equiv \mathrm{C}-\mathrm{H}$
[D] $\mathrm{H}-\mathrm{C} \equiv \mathrm{C}-(\mathrm{C}=\mathrm{O})-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{3}$
48. Arrange the following compounds in the increasing order of their reactivity towards $\mathrm{LiAlH}(\mathrm{O}-t-\mathrm{Bu})_{3}$
(i)

(ii)

(iii)

[A]
(i) < (ii) < (iii)
[B]
(iii) < (ii) < (i)
[C]
(ii) $<$ (iii) $<$ (i)
[D] (ii) < (i) < (iii)
49. The equivalent reagent for formyl anion synthon is
[A]

[B]

[C]

[D]

50. The most important peaks in the electron impact mass spectrum of 2-pentanone will be seen at $\mathrm{m} / \mathrm{z}$ values of:
[A] $15,29,43,58,71,86$
[B] $15,29,43,57,71,86$
[C] 15, 29, 43, 71, 86
[D] $15,29,57,71,86$
51. The products $\mathbf{X}$ and $\mathbf{Y}$ in the following reaction are, respectively,

[A]


[B]


[C]

$\mathbf{Y}=$

[D]
$X=Y=$

52. The major product obtained in the following reaction is

[A]

[B]

[C]

[D]

53. The major product formed in the following reaction is $\left(\mathrm{C}_{6} \mathrm{H}_{11}=\right.$ cyclohexyl $)$ :

[A]

[B]

[C]

[D]

54. The pair of major and minor products obtained in the following asymmetric induction is

[A]


[B]


[C]


[D]


55. Identify the major product obtained in the following reaction.

[A]

[B]

[C]

[D]

56. Predict the major product in the following transformation.

[A]

[B]

[C]

[D]

57. Identify the major products $\mathbf{X}$ and $\mathbf{Y}$ formed in the following reactions.

[A]

[B]

[C]


[D]

58. In which of the following reactions, nitrene is an intermediate?
(i) Schmidt rearrangement
(ii) Beckmann rearrangement
(iii) Curtius rearrangement
(iv) Stevens rearrangement
[A] (i) and (ii)
[B] (i) and (iii)
[C] (ii) and (iv)
[D] (iii) and (iv)
59. Match the starting materials with corresponding products of the following:
reactant

(a)
product

(i)

(b)

(ii)

(c)

(iii)
[A] (a) : (i), (b) : (ii), (c) : (iii)
[B] (a) : (ii), (b) : (iii), (c) : (i)
[C] (a) : (iii), (b) : (ii), (c) : (i)
[D] (a) : (ii), (b) : (i), (c) : (iii)
60. The major product $\mathbf{P}$ in the following reaction is


[A]

[C]

[B]

[D]

61. Among macrocycles I-IV, the anticrown and its affinity is for




III

[B] II and $\mathrm{Ag}^{+}$
[D] III and $\mathrm{Zn}^{2+}$
[A] I and $\mathrm{Na}^{+}$
62. Choose the best option for the photoexcitation of $\left[R u(b p y)_{3}\right]^{2+}$ to $\left[R u(b p y)_{3}\right]^{2+*}$ :
[A] $\left[\mathrm{Ru}(\mathrm{bpy})_{3}\right]^{2+*}$ is a good oxidizing agent
[B] $\left[\mathrm{Ru}(\mathrm{bpy})_{3}\right]^{2+*}$ is a good reducing agent
[C] $\left[\mathrm{Ru}(\mathrm{bpy})_{3}\right]^{2+*}$ is both a good oxidizing and also a good reducing agent
[D] $\left[\mathrm{Ru}(\mathrm{bpy})_{3}\right]^{2+*}$ becomes resistant to both oxidation and reduction
63. The name of the chemical process depicted in the following schematic diagram is

[A] Hydroformylation
[B] Fischer-Tropsch synthesis
[C] Water gas shift reaction
[D] Ziegler-Natta polymerization
64. Which one of the following organometallic complexes does not have bridging CO ligand(s)?
[A] $\mathrm{Ir}_{4}(\mathrm{CO})_{12}$
[B] $\mathrm{Os}_{4}(\mathrm{CO})_{15}$
[C] $\mathrm{Os}_{4}(\mathrm{CO})_{16}$
[D] $\mathrm{Co}_{4}(\mathrm{CO})_{12}$
65. Sulphur is isolobal with which of the following
[A] $\mathrm{Fe}(\mathrm{CO})_{4}$
[B] $\mathrm{Mn}(\mathrm{CO})_{4}$
[C] $\mathrm{Os}_{4}(\mathrm{CO})_{16}$
[D] $\mathrm{CH}_{2}{ }^{+}$
66. Which of the following statements are true for Photosystems-I and -II?
(i) $\mathrm{O}_{2}$ is produced by the photosystem-I
(ii) Mn cluster is involved in the water-splitting reaction of photosystem-II
(iii) Chlorophyll absorbs in the orange region of the electromagnetic spectrum.
(iv) The Mn cluster shuttles between cubane-like and adamantane-like configurations.
[A] (i), (ii) and (iv)
[B] (iii) and (iv)
[C] (i) and (ii)
[D] (ii) and (iv)
67. The coordination geometry associated with the following energy order of the d-orbitals $\mathrm{d}_{\mathrm{xz}}, \mathrm{d}_{\mathrm{yz}}<\mathrm{d}_{\mathrm{xy}}<\mathrm{d}_{\mathrm{z}}{ }^{2}<\mathrm{d}_{\mathrm{x}-\mathrm{y}}{ }^{2}{ }^{2}$ is
[A] trigonal
[B] square planar
[C] square pyramidal
[D] trigonal prismatic
68. Which of the following complex ions are expected to undergo tetragonal distortion? $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+},\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-},\left[\mathrm{MnF}_{6}\right]^{4-}$ and $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
[A] $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ and $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
[B] $\quad\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$ and $\left[\mathrm{MnF}_{6}\right]^{4-}$
[C] $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ and $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$
[D] $\left[\mathrm{MnF}_{6}\right]^{4-}$ and $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{6}\right]^{2+}$
69. The number of microstates and the ground term symbol for $\mathrm{Mn}^{4+}$ are
[A] 45 and ${ }^{3} \mathrm{~F}_{2}$, respectively.
[B] 120 and ${ }^{4} \mathrm{~F}_{3 / 2}$, respectively.
[C] 210 and ${ }^{5} \mathrm{D}_{0}$, respectively.
[D] 252 and ${ }^{6} \mathrm{~S}_{5 / 2}$, respectively.
70. Choose the correct statement for hydrogen azide:

(I)

(II)

(III)
[A] All of I-III contribute equally to the structure
[B] I is the least contributing structure
[C] II is the least contributing structure
[D] III is the least contributing structure
71. emf diagram for the standard half-cell reduction reaction in acid solution at $25^{\circ} \mathrm{C}$ is given below:

$$
\mathrm{E}^{\circ} \mathrm{Mn}^{3+} \xrightarrow{1.51 \mathrm{~V}} \mathrm{Mn}^{2+} \xrightarrow{-1.19 \mathrm{~V}} \mathrm{Mn}
$$

The $E^{0}$ value for the reaction $\mathrm{Mn}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Mn}$ is closest to
[A] $\quad-0.290 \mathrm{~V}$
[B] +0.290 V
[C] $\quad-0.107 \mathrm{~V}$
[D] +0.107 V
72. Which of the following correspond/s to inner sphere electron transfer process? [1,10phenanthroline $=$ Phen]
(i) $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}+\left[{ }^{*} \mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+} \rightarrow\left[{ }^{*} \mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}+\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
(ii) $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}+\left[{ }^{*} \mathrm{Fe}(\mathrm{Phen})_{3}\right]^{3+} \rightarrow\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}+\left[{ }^{*} \mathrm{Fe}(\mathrm{Phen})_{3}\right]^{2+}$
(iii) $\left[\mathrm{Pt}^{\mathrm{II}} \mathrm{Cl}_{4}\right]^{2-}+\left[* \mathrm{Pt}^{\mathrm{IV}} \mathrm{Cl}_{6}\right]^{2-} \rightarrow\left[\mathrm{Pt}^{\mathrm{IV}} \mathrm{Cl}_{6}\right]^{2-}+\left[{ }^{*} \mathrm{Pt}^{\mathrm{II}} \mathrm{Cl}_{4}\right]^{2-}$
[A] (i) and (ii)
[B] (i) and (iii)
[C] (iii) only
[D] (ii) only
73. Intramolecular racemization in octahedral $\left[\mathrm{Ni}(\mathrm{en})_{3}\right]^{2+}$ complex without loss of a ligand or breaking a bond
[A] can occur by twist along $\mathrm{C}_{3}$ axis
[B] can occur by twist along $\mathrm{C}_{2}$ axis
[C] can occur by twist along both $\mathrm{C}_{2}$ and $\mathrm{C}_{3}$ axes
[D] cannot occur by twist along either $\mathrm{C}_{2}$ and $\mathrm{C}_{3}$ axes
74. The metal active sites of the metalloenzymes carboxypeptidase, sulfite oxidase, aldehyde reductase and water oxidase, respectively, are
[A] copper, nickel, molybdenum and magnesium.
[B] molybdenum, zinc, cobalt and tungsten.
[C] nickel, manganese, tungsten and molybdenum.
[D] zinc, molybdenum, tungsten and manganese.
75. For a metal ion having a $S=3 / 2$ spin system, if the zero-field splitting parameter (D) is infinitely large compared to hv, the number of ESR transitions that would be observed is
[A] 3
[B] 1
[C] 2
[D] 4
76. Given that the ground and excited state nuclear energy levels of ${ }^{57} \mathrm{Fe}$ are $\mathrm{I}=1 / 2$ and $3 / 2$, the quadrupole splitting pattern in the Mössbauer spectrum of $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$ and $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$ ions are, respectively,

| [A] | 1 and 2 |
| :--- | :--- |
| [B] | 2 and 1 |
| [C] | 2 and 3 |
| [D] | 3 and 2 |

77. The geometry of $\mathrm{N}\left(\mathrm{CH}_{3}\right)_{3}$ is pyramidal, while $\mathrm{N}\left(\mathrm{SiH}_{3}\right)_{3}$ is a planar. This is due to:
[A] to overlapping of $\mathrm{p}_{\mathrm{Si}}$ and $\mathrm{p}_{\mathrm{N}}$ orbitals in $\mathrm{N}\left(\mathrm{SiH}_{3}\right)_{3}$
[B] valence shell electron pair repulsion in $\mathrm{N}\left(\mathrm{SiH}_{3}\right)_{3}$
[C] formation of resonance structure due to overlapping of $\mathrm{p}_{\mathrm{si}} \& \mathrm{~d}_{\mathrm{N}}$ orbitals in $\mathrm{N}\left(\mathrm{SiH}_{3}\right)_{3}$
[D] formation of resonance structures due to overlapping of $d_{S i} \& p_{N}$ orbitals in $\mathrm{N}\left(\mathrm{SiH}_{3}\right)_{3}$
78. A 50.00 mL of 0.0050 M NaCl solution is titrated with $0.0100 \mathrm{M} \mathrm{AgNO}_{3}$. Calculate pAg at 20 mL addition of $\mathrm{AgNO}_{3}$ and at equivalence point. The reaction is

$$
\mathrm{Ag}^{+}+\mathrm{Cl}^{-} \leftrightarrows \mathrm{AgCl}_{(\mathrm{s})}\left(\text { for } \mathrm{AgCl}, \mathrm{~K}_{s p}=1.82 \times 10^{-10}\right)
$$

[A] 4.87 and 6.79
[C] 0.05 and 0.1
[B] 1.82 and 14
[D] 6.59 and 4.87
79. An iron ore was analyzed by dissolving a 1.1324 g sample in concentrated HCl . The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $\mathrm{Fe}_{2} \mathrm{O}_{3} \cdot x \mathrm{H}_{2} \mathrm{O}$ by the addition of $\mathrm{NH}_{3}$. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure $\mathrm{Fe}_{2} \mathrm{O}_{3}(159.69 \mathrm{~g} / \mathrm{mol})$. The $\% \mathrm{Fe}$ ( $55.847 \mathrm{~g} / \mathrm{mol}$ ) in the sample is:
[A] 16.66
[B] 37.72
[C] 33.32
[D] 18.86
80. The structures of $\left[\mathrm{B}_{8} \mathrm{H}_{8}\right]^{2-},\left[\mathrm{B}_{9} \mathrm{H}_{9}\right]^{2-}$ and $\left[\mathrm{B}_{10} \mathrm{H}_{10}\right]^{2-}$ using Wade's rules, respectively, are
[A] dodecahedron, tricapped trigonal prism and bicapped square antiprism
[B] cube, tricapped trigonal prism and bicapped square prism
[C] bicapped octahedron, tricapped octahedron and bicapped square antiprism
[D] dodecahedron, tricapped trigonal prism and pentagonal bipyramid

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Note/Remarks :

