## Ph.D. Chemistry

## TIME: 2 HOURS

MAXIMUM MARKS: 70

## HALL TICKET NUMBER:

$\square$

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 1-26 are present (excluding 4 pages assigned for rough work).
3. There are eighty (80) multiple-choice questions in this paper ( $\mathbf{2 0}$ in Part-A and $\mathbf{6 0}$ in PartB). 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 $=6.022 \times 10^{23} ; \mathrm{amu}=1.674 \times 10^{-27} \mathrm{~kg}$.

## PART-A

1. Identify the most appropriate name reactions for conversion of (i) benzaldehyde into styrene and (ii) phenol into salicylaldehyde
[A] (i) Wittig reaction
[B] (i) Wittig reaction
(ii) Prins reaction
(ii) Reimer-Tiemann reaction
[C]
(i) Reimer-Tiemann reactioin
[D] (i) Reimer-Tiemann reaction
(ii) Wittig reaction
(ii) Prins reaction
2. The major product obtained in the following reaction is:



[C]


[D]

3. Identify the most appropriate reagent $(\mathrm{X})$ and the product $(\mathrm{Y})$ in the following reactions:

[A]
$X=P d / C$

[B]
$X=m$ CPBA; $Y=$

[C] $X=D D Q ; \quad Y=$

[D]

$$
X=D D Q ; \quad Y=
$$


4. Identify the species that can act as a 1,3-dipole in cycloadditions:
(i) $\mathrm{H}_{2} \mathrm{C}=\mathrm{N}_{2}$
(ii) $\mathrm{H}_{2} \mathrm{C}=\mathrm{C}=\mathrm{O}$
(iii) $\mathrm{O}_{3}$
(iv) $\mathrm{H}_{2} \mathrm{C}=\underset{\mathrm{H}}{\mathrm{C}}-\mathrm{OMe}$
[A] (ii) and (iii)
[B] (ii)
[C] (i), (ii) and (iv)
[D] (i) and (iii)
5. The major product formed in the following reaction is:

[A]

[B]

[C]

[D]

6. In Kiliani-Fischer synthesis of monosaccharides, the products are generally:
[A] Enantiomers
[B] Diastereomers
[C] Anomers
[D] Rotamers
7. The compound that shows the following mass spectrum is

[A]

[B]

[C]

[D]

8. The most significant observation of Watson and Crick that led to the proposal of the double helical model for DNA is:
[A] Hydrogen bonding between the
[B] Base stacking in the double helix nucleobases
[C] van der Waals attraction between nucleobases
[D] Electrostatic attraction between nucleobases
9. Hypophosphorous acid molecule has
[A] 4 lone pairs, $1 \pi$ bond and $5 \sigma$ bonds.
[B] 5 lone pairs and $5 \sigma$ bonds.
[C] 6 lone pairs, $1 \pi$ bond and $6 \sigma$ bonds.
[D] 7 lone pairs and $6 \sigma$ bonds.
10. The compound isolobal to $\mathrm{Ni}(\mathrm{CO})_{2}$ is:
$[\mathrm{A}] \quad\left[\mathrm{Co}(\mathrm{CO})_{4}\right]^{+}$
[B] $\mathrm{Fe}(\mathrm{CO})_{4}$
[C] $\left[\mathrm{Ni}(\mathrm{CO})_{3}\right]^{+}$
[D] $\left[\mathrm{Cu}(\mathrm{CO})_{2}\right]^{+}$
11. The lowest formal oxidation state of iron is found in
[A] $\left[\mathrm{CpFe}(\mathrm{CO})_{2}\right]_{2}$
[B] $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
[C] $\mathrm{Na}_{2}\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]$
[D] $\mathrm{Fe}(\mathrm{CO})_{5}$
12. Coulometry refers to:
[A] Determination of quantity of analyte using Faraday's law when the reaction proceeds at $100 \%$ current efficiency.
[B] Determination of quantity of analyte using half-wave potential.
[C] Qualitative determination of elements using half-wave potential.
[D] Quantitative determination of metals deposited on electrodes in a electrolytic process.
13. The metalloprotein oxyhemocyanin contains
[A] $\mathrm{Co}(\mathrm{II})$ and $\mathrm{O}_{2}{ }^{2-}$
[B] $\mathrm{Cu}(\mathrm{II})$ and $\mathrm{O}_{2}{ }^{2-}$.
[C] $\mathrm{Co}(\mathrm{IV})$ and $\mathrm{O}_{2}{ }^{-}$
[D] $\mathrm{Fe}(\mathrm{III})$ and $\mathrm{O}_{2}{ }^{2-}$
14. The most appropriate statement about valinomycin is:
[A] It is an acyclic oligopeptide capable of binding $\mathrm{K}^{+}$
[B] It is a cyclic oligopeptide capable of binding $\mathrm{K}^{+}$
[C] It is an acyclic oligopeptide capable of binding $\mathrm{Cl}^{-}$
[D] It is a cyclic oligopeptide capable of binding $\mathrm{Cl}^{-}$
15. Among $\mathrm{N}_{2}, \mathrm{H}_{2} \mathrm{O}, \mathrm{CH}_{3} \mathrm{CH}_{3}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, pure vibrational spectrum will be shown by
[A] $\mathrm{N}_{2}, \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$
[B] $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$
[C] $\mathrm{H}_{2} \mathrm{O}, \mathrm{CH}_{3} \mathrm{CH}_{3}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$
[D] $\mathrm{H}_{2} \mathrm{O}$
16. The commutator $2 \pi\left[x, p_{x}\right]$ equals to
[A] $i \hbar$
[B] $-i \hbar$
[C] $\quad i h$
[D] $-\hbar$
17. For a first-order reaction, $2 \mathrm{~A} \rightarrow$ Products, the expression for $[\mathrm{A}]$ is:
(Here, k : rate constant, t : time, $[\mathrm{A}]_{0}$ : initial concentration)
[A] $[\mathrm{A}]=[\mathrm{A}]_{0} \exp (-\mathrm{kt} / 2)$
[B] $\quad[\mathrm{A}]=2[\mathrm{~A}]_{0} \exp (-\mathrm{kt})$
[C] $[\mathrm{A}]=2[\mathrm{~A}]_{0} \exp (-2 \mathrm{kt})$
[D] $[\mathrm{A}]=[\mathrm{A}]_{0} \exp (-2 \mathrm{kt})$
18. The value of the rotational partition function for a structureless particle is:
[A] 0
[B] 1
[C] $\ln 2$
[D] Infinite
19. The single equivalent symmetry operation for $S_{6}^{3}$ is:
[A] $C_{3}$
[B] $\sigma_{h}$
[C] $E$
[D] $i$
20. The rotational symmetry number for water is:
[A] 0
[B] 1
[C] 2
[D] 3

## PART - B

21. Identify X and Y in the following reactions

[A]


[B]

$X=$


$$
Y=
$$


[C]



Z
[D]

$X=$


22. Identify X and Y in the following reactions

[A]

[B]



$$
B-6
$$

[C]


[D]


23. The major product formed in the following reaction is:

ii) Dess-Martin, DCM 4 hrs
iii) $\mathrm{NaClO}_{2}, \mathrm{NaH}_{2} \mathrm{PO}_{4}$ 2-methyl-2-butene
[A]

[B]

[C]

[D]

24. The major product obtained by the reaction of diphenylamine with benzoic acid in the presence of $\mathrm{ZnCl}_{2}$ at $230^{\circ} \mathrm{C}$ is:
[A]

[B]

[C]

[D]


$$
13-6
$$

25. The major product formed in the following reaction is:
26. $\mathrm{O}_{3},-78{ }^{\circ} \mathrm{C}, \mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{CH}_{3} \mathrm{OH}$
27. TsOH , rt
28. $\mathrm{NaHCO}_{3}, \mathrm{Me}_{2} \mathrm{~S}$
[A]

[B]

[C]

[D]

29. The biosynthetic precursor for the hormone serotonin and natural camphor respectively are:
[A] tryptophan and linaloyl pyrophosphate
[B] phenylalanine and neryl pyrophosphate
[C] glycine and chrysanthemyl pyrophosphate
[D] dopamine and farnesyl pyrophosphate
30. The major product formed in the following reaction is:

[A]

[B]

[C]

[D]

31. The reagents I and II in the following reactions are

[A] I $=\mathrm{CH}_{2} \mathrm{I}_{2}, \mathrm{Zn}-\mathrm{Cu} ; \mathrm{II}=\mathrm{Me}_{3} \mathrm{~S}^{+} \mathrm{I}^{-}, \mathrm{NaH}$
[B] $\mathrm{I}=\mathrm{CH}_{2} \mathrm{I}_{2}, \mathrm{Zn}-\mathrm{Cu} ; \mathrm{II}=\mathrm{Me}_{3} \mathrm{~S}^{+}(\mathrm{O}) \mathrm{I}^{-}, \mathrm{NaH}$
[C] I $=\mathrm{Me}_{3} \mathrm{~S}^{+}(\mathrm{O}) \mathrm{I}^{-}, \mathrm{NaH} ; \mathrm{II}=\mathrm{Me}_{3} \mathrm{~S}^{+} \mathrm{I}^{-}, \mathrm{NaH}$
[D] $\mathrm{I}=\mathrm{Me}_{3} \mathrm{~S}^{+}(\mathrm{O}) \mathrm{I}^{-}, \mathrm{NaH} ; \mathrm{II}=\mathrm{CH}_{2} \mathrm{I}_{2}, \mathrm{Zn}-\mathrm{Cu}$
32. The major product formed in the following reaction is:

[A]

[B]

[C]

[D]

33. The major product formed in the following reaction is:

[A]

[B]

[C]

[D]

34. The major product formed in the following reaction is:

[A]

[B]

[D]

35. The major product formed in the following reaction is:

[A]

[B]

[C]

[D]

36. The major product formed in the following reaction is:

[A]

[B]

[C]

[D]

37. The reaction intermediate involved in the following reaction is a

[A] singlet carbene
[B] radical
[C] carbanion
[D] triplet carbene
38. The relation between the benzylic protons (marked bold) in the following compounds I and II are respectively:


I


II
[A] homotopic and enantiotopic
[B] enantiotopic and enantiotopic
[C] enantiotopic and diastereotopic
[D] diastereotopic and enantiotopic
36. The major product formed in the following reaction is:

[A]

[C]



[D]


[B]

37. The major product formed in the following reaction is:

$$
\mathrm{CH}_{3} \mathrm{COOH} \xrightarrow{\substack{\text { i. } \mathrm{Br}_{2}, \mathrm{P} \\ \text { ii. } \mathrm{KCN}}}
$$

[A] Succinic acid
[B] Malonic acid
[C] Glycolic acid
[D] $\alpha$-Hydroxypropionic acid
38. The major product formed in the following reaction sequence is:

[A]

[B]

[C]

[D]

39. The major products $\mathbf{X}$ and $\mathbf{Y}$ formed in the following reactions are:

$$
\mathbf{x} \stackrel{\text { mCPBA, } \mathrm{CH}_{2} \mathrm{Cl}_{2}}{\mathrm{H}_{3} \mathrm{C} \underbrace{\mathrm{CH}_{3}}_{\mathrm{H}_{3} \mathrm{C}}} \xrightarrow{\begin{array}{l}
\text { (1) } \mathrm{Br}_{2}, \mathrm{H}_{2} \mathrm{O} \\
\text { (2) } \mathrm{KOH}, \mathrm{H}_{2} \mathrm{O}
\end{array}} \mathbf{Y}
$$

[A]

[B]

[C]

[D]

40. Identify the most appropriate chemical shifts (i to iv) to the labelled carbons (a to d) of the given compound from the following list:
Coles
(i) $\delta 25.7$
(ii) $\delta 38.1$
(iii) $\delta 129.8$
(iv) $\delta 150.9$
[A] a -(iv); b -(iii); c-(ii); d-(i)
[B] a-(iii); b-(iv); c-(ii); d-(i)
[C] a-(iv); b-(iii); c-(i); d-(ii)
[D] a-(iii); b-(iv); c-(i); d-(ii)
41. The experimental hydration energies of $\mathrm{Ca}^{2+}, \mathrm{Mn}^{2+}$ and $\mathrm{Zn}^{2+}$ were plotted against atomic numbers. A straight line passing through these points gave a value of $-716 \mathrm{kcal} / \mathrm{mol}$ as the hydration energy of $\mathrm{Ni}^{2+}$. If the ${ }^{3} \mathrm{~A}_{2 \mathrm{~g}} \rightarrow{ }^{3} \mathrm{~T}_{2 \mathrm{~g}}$ transition for $\left[\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ occurs at $8650 \mathrm{~cm}^{-1}$, calculate the expected hydration energy of $\mathrm{Ni}^{2+}\left[1 \mathrm{kcal} / \mathrm{mol}=350 \mathrm{~cm}^{-1}\right]$.
[A] $-666 \mathrm{kcal} / \mathrm{mol}$
[B] $-686 \mathrm{kcal} / \mathrm{mol}$
[C] $-746 \mathrm{kcal} / \mathrm{mol}$
[D] $\quad-766 \mathrm{kcal} / \mathrm{mol}$
42. Trigonal-bipyramidal complex of formula $\left[\mathrm{M}(\mathrm{A}-\mathrm{A}) \mathrm{B}_{2} \mathrm{X}\right]$ (A-A represents a symmetrical bidentate ligand and B and C represent two different monodentate ligands) can have
[A] 3 geometrical isomers and one of them will be optically active.
[B] 4 geometrical isomers and 2 of them will be optically active.
[C] 3 geometrical isomers and 2 of them will be optically active.
[D] 4 geometrical isomers and one of them will be optically active.
43. The correct styx number of $\left[\mathrm{B}_{10} \mathrm{H}_{15}\right]^{-}$structure given below is ( B in the given structure represents BH ):

[A] 3412
[B] 4012
[C] 3422
[D] 3622
44. Identify the correct order by using ${ }^{1} \mathrm{H}-\mathrm{NMR}$ chemical shift values of compounds.
[A] $\quad \mathrm{W}(\mathrm{Me})_{6}=\mathrm{Mn}(\mathrm{CO})_{5} \mathrm{H}<\left(\eta^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)_{2} \mathrm{Ni}<\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}$
[B] $\mathrm{Mn}(\mathrm{CO})_{5} \mathrm{H}<\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}<\left(\eta^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)_{2} \mathrm{Ni}<\mathrm{W}(\mathrm{Me})_{6}$
[C] $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}<\left(\eta^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)_{2} \mathrm{Ni}<\mathrm{W}(\mathrm{Me})_{6}<\mathrm{Mn}(\mathrm{CO})_{5} \mathrm{H}$
[D] $\mathrm{W}(\mathrm{Me})_{6}<\mathrm{Mn}(\mathrm{CO})_{5} \mathrm{H}<\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2} \mathrm{Fe}<\left(\eta^{2}-\mathrm{C}_{2} \mathrm{H}_{4}\right)_{2} \mathrm{Ni}$
45. Match the following terms:

| a | $\left(\eta^{1}-\mathrm{C}_{5} \mathrm{H}_{5}\right)\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)(\mathrm{CO})_{2} \mathrm{Fe}$ | i | Butterfly framework |
| :--- | :--- | :--- | :--- |
| b | $\mathrm{HCo}(\mathrm{CO})_{4}$ | ii | Hemocyanin |
| c | $\mathrm{Os}_{4}(\mathrm{CO})_{15}$ | iii | Ring Whizzer |
| d | Cyanide poisoning | iv | Carboxypeptidase |
| e | Arthropoda | v | Amyl nitrite |
| f | Entactic | vi | Acidic |

[A] $a=$ iii; $b=v i ; c=i ; d=v ; e=i i ; f=i v$
[B] $a=v i ; b=i ; c=i i i ; d=v ; e=i v ; f=i i$
[C] $a=v i ; b=v ; c=i ; d=i i ; e=i v ; f=i i i$
[D] $a=i i i ; b=v ; c=i ; d=i i ; e=i v ; f=v i$
46. The following diagrams are the pictorial representations of hemoglobin synthetic model systems.


The correct names of the models are:
[A] I) Roofed, II) Strapped and III) Picket fence
[B] I) Picket fence, II) Strapped and III) Roofed
[C] I) Picket fence, II) Roofed and III) Strapped
[D] I) Picket fence, II) Hemisphere and III) Roofed
47. The schematic drawing shown below represents active sites of bovin Superoxide Dismutase. X and Y are the metal centres.


Identify a combination of X and Y centres which can deactivate the enzyme.
[A] $\mathrm{X}=\mathrm{Zn}$ and $\mathrm{Y}=\mathrm{Cu}$
[B] $\mathrm{X}=\mathrm{Cu}$ and $\mathrm{Y}=\mathrm{Cu}$
[C] $\mathrm{X}=\mathrm{Co}$ and $\mathrm{Y}=\mathrm{Cd}$
[D] $\mathrm{X}=\mathrm{Cd}$ and $\mathrm{Y}=\mathrm{Cu}$
48. The rate of a substitution reaction is given by rate $=\left(k_{1}+k_{2}\left[\mathrm{I}^{-}\right]\right)\left[\mathrm{PtCl}(\text { dien })^{+}\right]$, with $k_{1}$ and $k_{2}$ being the first and second order rate constants. The observed rate in the presence of excess of $\mathrm{I}^{-}$ions is given by
[A] $k_{\mathrm{obs}}=k_{1}+k_{2}\left[\mathrm{I}^{-}\right]$
[B] $\quad k_{\mathrm{obs}}=k_{2}\left[\mathrm{I}^{-}\right]\left[\mathrm{PtCl}(\text { dien })^{+}\right]$
[C] $k_{\text {obs }}=k_{1}$
[D] $k_{\text {obs }}=k_{1}\left[\mathrm{PtCl}(\text { dien })^{+}\right]$
49. Consider Bailar twist and Ray-Dutt twist for the racemization of octahedral complexes with bidentate ligands and choose the correct statements among the following.
(i) Ray-Dutt twist takes place intermolecularly.
(ii) The $\mathrm{C}_{3}$ axis is the twist axis for Bailar twist.
(iii) Both the processes take place via a trigonal prismatic intermediate/transition state.
[A] (i) and (ii)
[B] (i) and (iii)
[C] (ii) and (iii)
[D] (ii) only
50. For the molecule $\mathrm{MX}_{7}$ with capped (capping on the square face) trigonal prismatic structure, how many environments are theoretically possible for X ?
[A] Two
[B] Three
[C] Four
[D] One
51. Given that $p\left[\mathrm{H}_{2}\right]=1, \mathrm{pH}=7,[\mathrm{Fe}]^{2+}=1 \mathrm{M}$, and $E_{\mathrm{Fe}}{ }^{2+} / \mathrm{Fe}=0.47 \mathrm{~V}$, the potential $E$ for the oxidation of Fe to $\mathrm{Fe}^{2+}$ is closest to
$[\mathrm{A}]+0.05 \mathrm{~V}$
[B] $\quad-0.05 \mathrm{~V}$
[C] -0.36 V
[D] $\quad+0.36 \mathrm{~V}$
52. Sulfur dioxide forms 1:1 coordination complexes with both $\mathrm{SbF}_{5}$ and $\operatorname{Ir}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{CO}) \mathrm{Cl}$. Choose the correct statement about the donor atom $\left(\right.$ from $\left.\mathrm{SO}_{2}\right)$ among the following.
[A] Oxygen is the donor atom in both the complexes.
[B] Sulfur is the donor atom in both the complexes.
[C] Sulfur is the donor atom in the iridium complex and the oxygen is the donor atom in $\mathrm{SbF}_{5}$ complex.
[D] Oxygen is the donor atom in the iridium complex and sulfur is the donor atom in the $\mathrm{SbF}_{5}$ complex.
53. Consider a metal ion having a $S=3 / 2$ spin system. Predict the possible number of fine structures in an EPR spectrum if you consider a zero field splitting ZFS (D) and Kramer's degeneracy to be present in the system and in case if the ZFS (D) value is too large compared to applied magnetic field.
[A] 3 and 1, respectively.
[B] 4 and 2, respectively.
[C] 1 and 2 , respectively.
[D] 3 and 2 , respectively.
54. For $\mathrm{Sm}^{3+}$ and $\mathrm{Eu}^{3+}$, the calculated values of $\mu_{\mathrm{J}}(\mathrm{BM})$ are far lesser than the experimentally obtained values of 1.6 and 3.6 BM respectively. The reason for this anamoly is
[A] multiplet width approximately being equal to $\mathrm{k}_{\mathrm{B}} \mathrm{T}$.
[B] multiplet width much lesser than $\mathrm{k}_{\mathrm{B}} \mathrm{T}$.
[C] multiplet width greater than $\mathrm{k}_{\mathrm{B}} \mathrm{T}$.
[D] multiple width infinitely larger than $\mathrm{k}_{\mathrm{B}} \mathrm{T}$.
55. Identify the $d^{\mathrm{n}}$ system corresponding to the Tanabe-Sugano configuration given below. Also identify the number of spin allowed transitions in the weak and strong field part of the diagram.

[A] $d^{4}: 2$ and 1 , respectively.
[B] $d^{5}: 3$ and 3 , respectively.
[C] $d^{6}: 1$ and 4, respectively.
[D] $d^{\top}: 3$ and 1 , respectively.
56. Calculate the cell potential for
$\mathrm{Ag} \mid \mathrm{AgCl}$ (saturated) $, \mathrm{HCl}(0.0200 \mathrm{M}) \mid \mathrm{H}_{2}(0.800 \mathrm{~atm}), \mathrm{Pt}$
and comment whether it is a spontaneous (galvanic cell) or non-spontaneous (electrolytic cell) reaction (Use $E_{\text {AgCl/Ag }}^{o}=0.222 \mathrm{~V}$ )
[A] 0.00 V and no reaction will occur
[B] -0.420 and non-spontaneous electrolytic cell
[C] +0.420 and spontaneous galvanic cell
[D] +0.222 V and non-spontaneous electrolytic cell
57. For the electron transfer process $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{X}\right]^{2+}+\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+5 \mathrm{H}_{3} \mathrm{O}^{+} \rightarrow\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{X}\right]^{2+}$ $+\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+5 \mathrm{NH}_{4}{ }^{+}$, identify the correct pair of inert complexes:
[A] $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{X}\right]^{2+}$ and $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
[B] $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{X}\right]^{2+}$ and $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
[C] $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{X}\right]^{2+}$ and $\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$
[D] $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{X}\right]^{2+}$ and $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{X}\right]^{2+}$
58. Among macrocycles $\mathrm{A}, \mathrm{B}$ and C , the order of affinity towards lithium ion is

A

B

C
[A] $\mathrm{C}=\mathrm{B}=\mathrm{A}$
[B] A $<$ B $<$ C
[C] $\mathrm{C}<\mathrm{B}<\mathrm{A}$
[D] $\mathrm{C}<\mathrm{A}<\mathrm{B}$
59. Truncated icosahedron (e.g., $\mathrm{C}_{60}$ ) has
[A] 12 pentagons and 20 hexagons
[B] 12 pentagons and 20 squares
[C] 20 equilateral triangular faces and 20 hexagons
[D] 20 equilateral triangular faces and 12 pentagons

60 . Which statement among the following about a Verkade's superbase is correct?
[A] Protonation occurs on the phosphorus atom with additional intramolecular $\mathrm{N}-\mathrm{P}$ bond formation
[B] Protonation occurs on the phosphorus atom without any additional intramolecular $\mathrm{N}-\mathrm{P}$ bond formation
[C] Protonation occurs on the nitrogen atom without any additional intramolecular N-P bond formation
[D] Protonation occurs on the nitrogen atom with the additional intramolecular $\mathrm{N}-\mathrm{P}$ bond formation
61. The packing efficiency of a 2 -dimensional square lattice is:
[A] 0.820
[B] 0.785
[C] 0.682
[D] 0.750
62. The bond dissociation energy of $\mathrm{H}_{2}$ molecule is $431.6 \mathrm{~kJ} \mathrm{~mol}^{-1}$. If the zero-point energy of $\mathrm{H}_{2}$ molecule is $26.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$, the bond-dissociation energy of $\mathrm{D}_{2}$ molecule in $\mathrm{kJ} \mathrm{mol}^{-1}$ is: (assume identical force constant for the $\mathrm{H}-\mathrm{H}$ and D-D bonds)
[A] 457.6
[B] 405.6
[C] 439.2
[D] 444.1
63. The reaction $2 \mathrm{NO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$ proceeds through the following steps:

$$
\begin{aligned}
& 2 \mathrm{NO} \underset{\mathrm{~N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2}}{\rightleftharpoons} \rightarrow \underset{2}{\stackrel{\mathrm{NO}_{2} \mathrm{O}_{2}}{2}} \text { (fast) }
\end{aligned}
$$

If $\Delta \mathrm{G}$ for the first step is $-15 \mathrm{kcal} \mathrm{mol}^{-1}$ and $E_{a}$ for the second step is $9 \mathrm{kcal} \mathrm{mol}^{-1}$, the rate constant of the reaction at $35^{\circ} \mathrm{C}\left(\mathrm{k}_{2}\right)$ is related to the rate constant at $25^{\circ} \mathrm{C}\left(\mathrm{k}_{1}\right)$ as
[A] $\mathrm{k}_{2}=8.2 \mathrm{k}_{1}$
[B] $\mathrm{k}_{2}=0.6 \mathrm{k}_{1}$
[C] $\mathrm{k}_{2}=7.2 \mathrm{k}_{1}$
[D] $\mathrm{k}_{2}=6.3 \mathrm{k}_{1}$
64. The characters of the irreducible representations of $C_{3 h}$ point group are given below. The correct Mulliken symbols for the $I R_{1}$ and $\mathrm{IR}_{2}$ are:

| $C_{3 h}$ | $E$ | $2 C_{3}$ | $\sigma_{h}$ | $2 S_{3}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{IR}_{1}$ | 2 | -1 | 2 | -1 |
| $\mathrm{IR}_{2}$ | 1 | 1 | -1 | -1 |

[A] $E$ and $A$
[B] $E^{\prime}$ and $A^{\prime \prime}$
[C] $E^{\prime \prime}$ and $A^{\prime}$
[D] $E_{2}$ and $A_{1}$
65. The separation between the energy levels in a two-level system is $1.38 \times 10^{-20} \mathrm{~J}$. The temperature (in K ) at which the population of the ground state would be 4 times greater than that of the excited state is closest to:
[A] 475
[B] 530
[C] 721
[D] 1220
66. The rotational temperature for $\mathrm{H}_{2}$ with a rotational constant $60.6 \mathrm{~cm}^{-1}$ is nearly equal to:
[A] 67.3
[B] 77.3
[C] 87.3
[D] 97.3
67. The work done (in $k J$ ) when 3 moles of an ideal monatomic gas at 298 K undergo irreversible isothermal expansion from pressure of 60.0 kPa to 30.0 kPa until the volume is doubled is:
[A] 0.37
[B] 3.7
[C] -0.37
[D] -3.7
68. The bond length in ${ }^{12} \mathrm{C}^{14} \mathrm{~N}$ is 117 pm , and its force constant is $1630 \mathrm{Nm}^{-1}$, the fundamental vibrational frequency (in $\mathrm{cm}^{-1}$ ) is:
[A] $2.07 \times 10^{3}$
[B] $2.07 \times 10^{2}$
[C] $3.07 \times 10^{3}$
[D] $2.07 \times 10^{2}$
69. The zero-point energy (in J) of an electron confined in a box of length 1.0 nm is close to:
[A] $1.060 \times 10^{-20}$
[B] $4.025 \times 10^{-20}$
[C] $6.025 \times 10^{-20}$
[D] $3.025 \times 10^{-20}$
70. The correct expression for the Langmuir adsorption isotherm which is required to plot the experimental data set of pressure and volume is (where $V_{\infty}$ is the volume corresponding to complete coverage and $K$ is the ratio of adsorption and desorption rate constants):
[A] $\frac{p}{V}=\frac{p}{V_{\infty}}-\frac{1}{K V_{\infty}}$
[B] $\frac{p}{V}=\frac{p}{V_{\infty}}+\frac{1}{K}$
[C] $\frac{p}{V}=\frac{p}{V_{\infty}}+\frac{1}{K V_{\infty}}$
[D] $\frac{p}{V}=\frac{p}{V_{\infty}}-\frac{1}{K}$
71. The polymer molecular weight vs. conversation plots of two different polymerization mechanisms are shown below. Plots (A) and (B) represent:


[A] step and chain polymerizations, respectively
[B] chain polymerization of different types
[C] chain and step polymerizations, respectively
[D] step polymerization of different types
72. The reduced form of the van der Waals equation is:
[A] $p_{r}=\frac{8 T_{r}}{3 V_{r}-1}-\frac{3}{T_{r} V_{r}^{2}}$
[B] $p_{r}=\frac{8 T_{r}}{3 V_{r}-1}-\frac{3}{V_{r}^{2}}$
[C]
$p_{r}=\frac{3 T_{r}}{8 V_{r}-1}-\frac{8}{3 T_{r} V_{r}^{2}}$
[D] $p_{r}=\frac{3 V_{r}}{8 T_{r}-1}-\frac{3}{V_{r}^{2}}$
73. Which of the following is equal to zero:
[A] $\left[\hbar L_{z}, L^{2}\right]$
[B] $\left[L_{Z}, \hbar L\right]$
[C] $\left[L_{x}, i L_{y}\right]$
[D] $\left[L_{y}, i L_{z}\right]$
74. The energy eigenvalue of the ground electronic state of a hydrogen atom is -13.6 eV . If the atom stays in this state for 2 ns , the uncertainty in its energy (in eV ) will be close to
[A] $1.64 \times 10^{-7}$
[B] $5.23 \times 10^{-7}$
[C] $8.23 \times 10^{-7}$
[D] $6.14 \times 10^{-7}$
75. The spatial part of the ground electronic wave function of $\mathrm{H}_{2}$ molecule is given by $\Psi=\mathrm{N}$ $\left[1 \mathrm{~s}_{\mathrm{A}}(1)+1 \mathrm{~s}_{\mathrm{B}}(1)\right]\left[1 \mathrm{~s}_{\mathrm{A}}(2)+1 \mathrm{~s}_{\mathrm{B}}(2)\right]$, where the two hydrogen atoms are designated by A and $\mathrm{B}, 1$ and 2 are the two electrons, and N is the normalization constant. The term symbol of the corresponding electronic state is:
[A] ${ }^{1} \Sigma_{g}^{+}$
[B] ${ }^{1} \Sigma_{u}^{-}$
[C]. ${ }^{3} \Sigma_{g}^{+}$
[D] ${ }^{3} \Sigma_{u}^{+}$
76. Butadiene has an absorption at $4.54 \times 10^{4} \mathrm{~cm}^{-1}$ for an electron on a transition from $n=2$ state to $n=3$ state. Assuming that butadiene can be modeled as a particle in a 1 dimensional box, the approximate total length of the molecule (in $\AA$ ) is:
[A] 5.78
[B] 4.78
[C] 6.78
[D] 7.78
77. If $4 \%$ of the $\mathrm{K}^{+}$ions in a KCl crystal are replaced by $\mathrm{Ca}^{2+}$ ions, the $\%$ decrease in the density of the crystal [atomic weight $\left(\mathrm{g} \mathrm{mol}^{-1}\right): \mathrm{K}=39.10 ; \mathrm{Ca}=40.08 ; \mathrm{Cl}=35.45$ ] is:
[A] 0.00
[B] 0.50
[C] 1.02
[D] 2.05
78. In the X-ray diffraction pattern of a crystal with a cubic lattice, peaks are observed at $2 \theta$ values of $21.00^{\circ}$ and $29.87^{\circ}$. If the first peak is assigned to the ( 100 ) plane, the second peak can be assigned to the plane:
[A] ( $\left.\begin{array}{lll}1 & 1 & 0\end{array}\right)$
[B] $\left(\begin{array}{lll}1 & 1 & 1\end{array}\right)$
[C] ( $\left.\begin{array}{lll}\overline{1} & 0 & 0\end{array}\right)$
[D] (200)
79. The ionic mobility of $\mathrm{Na}^{+}$ion (in $\mathrm{m}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$ ) in 0.1 M aqueous solution of NaCl at $25^{\circ} \mathrm{C}$, (given the diffusion coefficient of $\mathrm{Na}^{+}$ion is $1.30 \times 10^{-9} \mathrm{~m}^{2} \mathrm{~s}^{-1}$ ) is:
[A] $5.92 \times 10^{-7}$
[B] $0.59 \times 10^{-7}$
[C] $5.06 \times 10^{-8}$
[D] $50.6 \times 10^{-8}$
80. A zinc rod is placed in 0.1 M solution of zinc sulphate at $25^{\circ} \mathrm{C}$. Assume that the salt is dissociated to the extent of $95 \%$ at this dilution. Given, $E_{Z n^{2+}, Z n}^{0}=-0.76 \mathrm{~V}$, the electrode potential (in V ) at $25^{\circ} \mathrm{C}$ is:
[A] -0.79
[B] 0.79
[C] -0.76
[D] 0.76

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