# ENTRANCE EXAMINATIONS - 2023 

(Ph.D. Admissions - January 2024 Session)

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 1-25 are present (excluding 5 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 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.

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c-10
$$

## Useful Constants:

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

## PART-A

1. Which of the following changes in a ${ }^{1} \mathrm{H}$ NMR spectrum of a molecule would indicate weakening of intramolecular hydrogen bonding?
[A] Upfield chemical shift
[B] Line broadening
[C] Downfield chemical shift
[D] Appearance of dispersive lineshape
2. Which of the following is not an example of a state function?
[A] Change in Gibbs free energy
[B] Change in entropy
[C] Change in enthalpy
[D] Work done
3. A solid state property that does not change with temperature is
[A] Energy gap of a superconductor
[B] Paramagnetic susceptibility
[C] Diamagnetic susceptibility
[D] Thermal conductivity
4. Light emission from a LED arises due to
[A] a chemical reaction in the device
[B] heating of the solid element
[C] photo-excitation of electrons
[D] electron-hole recombination
5. The limiting molar conductivity of $\mathrm{NaOH}, \mathrm{NaF}$ and $\mathrm{NH}_{4} \mathrm{~F}$ are $24.8,10.5$ and $12.5 \mathrm{mS} \mathrm{m}^{2}$ $\mathrm{mol}^{-1}$ respectively. The limiting molar conductivity of $\mathrm{NH}_{4} \mathrm{OH}$ would be close to (in unit of $\mathrm{mS} \mathrm{m} \mathrm{mol}^{-1}$ )
[A] 29.1
[B] 26.8
[C] 10.7
[D] 15.9
6. Molecules of two gases, A and B are adsorbed on a solid at adjoining sites react. If A is adsorbed very strongly compared to B , the reaction rate is proportional to: ( $p_{A}$ and $p_{B}$ are the partial pressure of A and B , respectively)
[A] $p_{A}$
[B]
$\frac{p_{B}}{p_{A}}$
[C] $\frac{p_{A}}{p_{B}}$
[D]
$p_{A} p_{B}$
7. If the critical volume of a van der Wails gas is $148 \mathrm{~cm}^{3} \mathrm{~mol}^{-1}$, the radius (in $\AA$ ) of the gas molecule is
[A] 1.94
[B] 3.88
[C] 0.97
[D] 4
8. The product obtained from the methanolysis of the below compound is

[A]

[B]

[C]

[D]

9. The best reagents for synthesis of indole-3-carboxaldehyde and further its conversion into 3-(2-nitrovinyl)indole, respectively are
[A] $\mathrm{CHCl}_{3}, \mathrm{NaOH}$, ethanol and $\mathrm{CH}_{3} \mathrm{NO}_{2} / \mathrm{NH}_{4} \mathrm{OAc}$
[B] DMF/POCl ${ }_{3}$ and $\mathrm{CH}_{3} \mathrm{NO}_{2} / \mathrm{NH}_{4} \mathrm{OAc}$
[C] $\mathrm{CHCl}_{3}, \mathrm{NaOH}$, ethanol and $\mathrm{HOOCCH}_{2} \mathrm{NO}_{2} /$ pyridine
[D] $\mathrm{CO}+\mathrm{HCl}, \mathrm{ZnCl}_{2}$ and $\mathrm{HOOCCH}_{2} \mathrm{NO}_{2} /$ pyridine
10. The biosynthetic precursors for the hormone, serotonin and natural camphor respectively are
[A]
[B]
[C]
[D]

Tryptophan and linaloyl pyrophosphate.
Phenylalanine and neryl pyrophosphate.
Glycine and chrysanthemyl pyrophosphate.
Dopamine and farnesyl pyrophosphate.
11. The major product obtained in the following reaction is

[A]

[B]

[C]

[D]

12. Identify the absolute stereochemistry (IUPAC) of (i) and (ii), respectively

(i)

(ii)
[A] i-(R); ii-(S)
[B] i-(S); ii-(R)
[C] i- $(R)$; ii- $(R)$
[D] i-(S); ii-(S)
13. The compound having a higher barrier for rotation about the marked bond is:
[i]

[ii]

[iii]

[iv]

[A] i
[B] ii
[C] iii
[D] iv
14. Predict the product in the following reaction.

[A]

[B]

[C]

[D]

15. Magnetic moment of $\mathrm{Dy}^{3+}$ ion would be
[A] 10.63 BM
[B] 9.72 BM
[C] 9.59 BM
[D] 7.94 BM
16. The number of triangular faces in square pyramid and trigonal bipyramid are, respectively
[A] 6 and 4
[B] 5 and 5
[C] 4 and 6
[D] 6 and 5
17. Choose the correct statement for $\mathrm{BF}_{3}$ and $\mathrm{CO}_{3}{ }^{2-}$.
[A] Both are isoelectronic and isostructural.
[B] Both are isoelectronic but not isostructural.
[C] Both are not isoelectronic but isostructural.
[D] Both are neither isoelectronic nor isostructural.
18. The correct set of biologically essential element is
[A] $\mathrm{Fe}, \mathrm{Mo}, \mathrm{Cu}, \mathrm{Zn}$.
[B] $\mathrm{Fe}, \mathrm{Cu}, \mathrm{Co}, \mathrm{Ru}$.
[C] $\mathrm{Cu}, \mathrm{Mn}, \mathrm{Zn}, \mathrm{Ag}$.
[D] $\mathrm{Fe}, \mathrm{Ru}, \mathrm{Zn}, \mathrm{Mg}$.
19. Starting with an initial quantity of 0.070 mole for ${ }^{222} \mathrm{Rn}_{86}$ (half-life $=3.8$ days), how much of it is present after 16 days?
[A] 0.0038 .
[B] 0.0056 .
[C] 0.0092 .
[D] 0.0380 .
20. Identify the option in which both electron transfer and energy transfer occur (i) ferredoxin (ii) chlorophyll (iii) cytochromes and (iv) photosystem
[A]
(ii) and (iii)
[B] (iv)
[C]
(i), (ii), (iii) and (iv)
[D] (i) and (iv)

## PART-B

21. If the ${ }^{1} \mathrm{H}$ resonance frequency in a 1 T magnetic field is 42.577 MHz , the resonance frequency $(\mathrm{MHz})$ for ${ }^{31} \mathrm{P}$ nucleus in the same magnetic field is closest to: (Gyromagnetic ratio $\gamma$ for ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}$ nuclei are $26.752 \times 10^{7}$ and $10.841 \times 10^{7} \mathrm{rad} \mathrm{T}^{-1} \mathrm{~s}^{-1}$, respectively)
[A] 10.644
[B] 14.192
[C] 17.258
[D] 21.288
22. Neon gas (assumed to be ideal) at an initial temperature of 250 K is expanded reversibly and adiabatically from a volume of 100 L to 500 L . The final temperature (in K ) is
[A] 85
[B] 100
[C] 147
[D] 735
23. When 6 g of a substance is dissolved in 500 g of benzene at 298 K , the boiling point rises by 0.65 K , the freezing point depression (in K$)$ is: $\left(\mathrm{K}_{\mathrm{f}}=5 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}, \mathrm{~K}_{\mathrm{b}}=2.5 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-}\right.$ ${ }^{1}$ )
[A] -0.33
[B] -1.3
[C] 0.33
[D] 1.3
24. The vibrational frequency of a diatomic molecule $A-B$ is $v$. If a molecule $C$-D has the same force constant as $A-B$ and the mass of $C$ and $D$ are respectively twice that of $A$ and $B$, the vibrational frequency of $C-D$ is
[A] $2 v$
[B] $\sqrt{2} v$
[C] $v / \sqrt{2}$
[D] $4 v$
25. In a first order reaction, the concentration of the reactant decreased to $25 \%$ of the initial value in 375 s ; the rate constant (in $\mathrm{s}^{-1}$ ) is
[A] $3.696 \times 10^{-3}$
[B] $2.93 \times 10^{-3}$
[C] $1.848 \times 10^{-3}$
[D] $1.465 \times 10^{-3}$
26. Which of the following relationship is correct for a particle in one-dimensional box of length $a$
[A] $\frac{\langle E\rangle}{\left\langle p^{2}\right\rangle}=\frac{1}{2 m}$
[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] $\frac{\langle E\rangle}{\langle p\rangle}=\frac{h^{2}}{2 m}$
27. The rate constant of a reaction at $30^{\circ} \mathrm{C}$ is exactly twice the value at $20^{\circ} \mathrm{C}$. The activation energy of the reaction (in $\mathrm{kJ} \mathrm{mol}^{-1}$ ) is closest to
[A] 35.2
[B] 42.3
[C] 51.2
[D] 72.1
28. The ground state of a $\mathrm{ClO}_{2}$ molecule ( $\mathrm{C}_{2 \mathrm{v}}$ point group) trapped in a solid is known to be of $\mathrm{B}_{1}$ symmetry. Light polarized parallel to the Y-axis excites the molecule to an upper electronic state; the symmetry of the excited state is: (the character table of the $\mathrm{C}_{2 \mathrm{v}}$ point group is given below)

| $C_{2 v}$ | E | $\mathrm{C}_{2}$ | $\sigma_{v}(x z)$ | $\sigma_{v}(y z)$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $A_{1}$ | 1 | 1 | 1 | 1 | z |
| $A_{2}$ | 1 | 1 | -1 | -1 |  |
| $B_{1}$ | 1 | -1 | 1 | -1 | x |
| $B_{2}$ | 1 | -1 | -1 | 1 | y |

[A] $A_{1}$
[B] $A_{2}$
[C] $B_{1}$
[D] $B_{2}$
29. 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 time $t,(\mathrm{P}(t))$, is related to the rate constants and initial concentration, $[\mathrm{A}]_{0}$ as (where, $k=k_{1}+k_{2}$ )
[A] $\quad \mathrm{P}(t)=k_{1}[\mathrm{~A}]_{0}\left(1-e^{-k_{1} t}\right)$
[B] $\quad \mathrm{P}(t)=k_{1}[\mathrm{~A}]_{0}\left(1-e^{-k t}\right)$
[C]
$\mathrm{P}(t)=k_{1}[\mathrm{~A}]_{0}\left(1-e^{-k_{1} t}\right) / k_{2}$
[D] $\quad \mathrm{P}(t)=k_{1}[\mathrm{~A}]_{0}\left(1-e^{-k t}\right) / k$
30. A crystal with a body-centred cubic lattice is made up of atoms having a radius of $2.0 \AA$. The free volume in the unit cell of this crystal (in $\AA^{3}$ ) is
[A] 8
[B] 31.5
[C] 32.3
[D] 65.0
31. A non-stoichiometric compound is formed by replacing $10 \%$ of $\mathrm{Zr}^{4+}$ ions in $\mathrm{ZrO}_{2}$ by $\mathrm{Ca}^{2+}$ ions, maintaining charge neutrality of the solid. The percentage of $\mathrm{O}^{2-}$ defects created is
[A] 5
[B] 10
[C] 15
[D] 20
32. The variation of surface pressure with area occupied by three different surfactant molecules is shown below. Among the three surfactants (stearic acid, isostearic acid and tri-p-cresyl phosphate) the molecule with the highest collapse pressure is

[A] Tri- $p$-cresyl phosphate
[B] Isostearic acid
[C] Stearic acid
[D] All three have similar collapse pressure
33. If the change of surface tension with concentration at constant temperature, $\left(\frac{\partial \gamma}{\partial \ln c}\right)_{T}$, of a fatty acid is $-40 \mu \mathrm{~N} \mathrm{~m}^{-1}$. At $20^{\circ} \mathrm{C}$, the number of fatty acid molecules present per square meter of the surface in a $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ aqueous solution is
[A] $\quad 9.6 \times 10^{15}$
[B] $9.6 \times 10^{11}$
[C] $\quad 19.2 \times 10^{15}$
[D] $19.2 \times 10^{11}$

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34. At 298 K , the standard electrode potentials for the half-cells are given below.

$$
\begin{array}{cl}
\mathrm{Pd}^{2+}(\mathrm{aq})+2 e^{-} \rightleftharpoons \mathrm{Pd}(\mathrm{~s}) & E^{0}=0.83 \mathrm{~V} \\
\mathrm{PdCl}_{4}^{2-}(\mathrm{aq})+2 e^{-} \rightleftharpoons \mathrm{Pd}(\mathrm{~s})+4 \mathrm{Cl}^{-}(\mathrm{aq}) & E^{0}=0.64 \mathrm{~V}
\end{array}
$$

At 298 K , the equilibrium constant for the reaction is closest to:

$$
\mathrm{Pd}^{2+}(\mathrm{aq})+4 \mathrm{Cl}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{PdCl}_{4}^{2-}(\mathrm{aq})
$$

[A]
$1.4 \times 10^{6}$
[B]
$2.8 \times 10^{6}$
[C]
$5.6 \times 10^{6}$
[D]
$7.6 \times 10^{6}$
35. The normalization factor for the wave function of a particle in one-dimensional box of length $a$ is
[A]
$\sqrt{a / 2}$
[B]
[D]
$\sqrt{2 / a}$
[C]
$\sqrt{a / \pi}$
$\sqrt{a / \pi}$
36. The gap between the two energy levels in a two-level system is $100 \mathrm{~cm}^{-1}$. The temperature at which the population of the upper state becomes one-fourth of that in the lower state is nearly equal to (in K )
[A] 260
[B] 520
[C] 1040
[D] 2080
37. With the 4 -fold increase of temperature, the factor by which the translational partition function of a gas increases (assuming the volume of the container remains the same) is:
[A] 2
[B] 4
[C] 6
[D] 8
38. Equal weights of polymers with molecular weights $10,000 \mathrm{~g} \mathrm{~mol}^{-1}$ and $100,000 \mathrm{~g} \mathrm{~mol}^{-1}$ is mixed. The weight average molecular weight $\left(\mathrm{g} \mathrm{mol}^{-1}\right)$ is
[A] $2.75 \times 10^{4}$
[B] $2.75 \times 10^{3}$
[C] $5.5 \times 10^{4}$
[D] $5.5 \times 10^{3}$
39. The standard electrode potential and the temperature coefficient for a cell are 2 V and $-5 \times 10^{-4} \mathrm{~V} / \mathrm{K}$, respectively. Considering involvement of 2 electrons in the cell reaction, the standard reaction enthalpy at 300 K is closest to (in kJ )
[A] +206
[B] -413
[C] -193
[D] +354
40. At 200 nm , the transmittance of a $1.42 \times 10^{-3} \mathrm{M}$ solution of a chemical compound is 0.083 . If the path length of the cell is $1.21 \times 10^{-3} \mathrm{~m}$, the value of molar absorption coefficient (in $\mathrm{m}^{2} \mathrm{~mol}^{-1}$ ) is closest to
[A] 6.28
[B] 1.29
[C] 628
[D] 329
41. Predict the major product in the following reaction.


iii. $\mathrm{H}_{3} \mathrm{O}^{+}$
[A]

[B]

[C]

[D]

42. Predict the major product in the following transformation.

[A]

[B]

[C]

[D]

43. Identify the product in the following reaction

[A]

[B]

[C]

[D]

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

[A]

[B]

[C]


[D]


45. Identify X and Y in the following reaction sequence.


$\gamma=$

[C] $x=$


 $Y=$

[D] x
 $Y=$


$$
C-1 \sigma
$$

46. Identify X and Y in the following reaction sequence

[A] C

[B] $X=$

[C] $X=$


[D] $X=$

$Y=$

47. The major product formed in the following reaction is

[A]

[B]

[C]

[D]

48. Identify the products X and Y in the following transformations


[A]
$Y=$

[B]

[C]


[D]



49. The major product formed in the following reaction is

[A]

[B]

[C]

[D]

50. The major product formed in the following reaction is

[A]

[B]

[C]

[D]

51. The major product of the following reaction is:

[A]

[B]

[C]

[D]

52. Identify the major products X and Y formed in the following reactions:

[A]

[B]

[C]

[D]

53. Identify the major products X and Y formed in the following reactions:

[A]

[B]

[C]

[D]


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54. The appropriate matching of the $\mathrm{k}_{\mathrm{H}} / \mathrm{k}_{\mathrm{D}}$ values for the given reactions (1), (2) and (3) respectively are



[A] 2.70, 4.90, 0.37
[B] $0.37,4.90,2.70$
[C] 4.90, 0.37, 2.70
[D] 2.70, 0.37, 4.90
55. Find out the product in the reaction given below.

[A]

[B]

[C]

[D]

56. Find out the product in the following transformation.

[A]

[B]

[C]

[D]

57. The provided mass spectrum corresponds to a compound having the molecular formula $\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}$. The compound is

[A] Butyraldehyde
[C] Tetrahydrofuran
[B] Butan-2-one
[D] Cyclobutanol
58. Identify the compound associated with the provided IR spectrum.

[A]

[B]

[C]

[D]

59. The NMR spectrum of Compound $\mathrm{A}\left(\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{O}_{2}\right)$ reveals resonances at $\delta 1.4,2.25$ and 3.9 with an intensity ratio of $6: 3: 1$. Select the most probable structure for Compound A from the provided options.
[A] 1-hydroxy, 3-methyl-butan-2-one
[B] 3-hydroxy, 3-methyl-butan-2-one
[C] 1-hydroxy-pentane-3-one
[D] 2-hydroxy-pentan-3-one

60. Select the reaction that calix[4]pyrrole undergoes easily?

[A] Planar complexation with tetravalent metal ions by deprotonation
[B] Planar complexation with anions by hydrogen bonding
[C] 1,3-alternate arrangement of pyrrole ring and complexation with tetravalent metal ions by deprotonation
[D] Complexation with anions in cone conformation by hydrogen bonding
61. The correct statement when molecule $A$ is photoexcited to $A^{*}$
[A] $A^{*}$ is a good oxidizing agent
[B] $A^{*}$ is a good reducing agent
[C] $\mathrm{A}^{*}$ is both a good oxidizing and also a good reducing agent
[D] Both A and A* are equally good oxidants and reductants
62. Which element among the Group 15 elements can display $a+1$ oxidation state, and what is the reason?
[A] Nitrogen, due to the absence of ' $d$ ' orbital
[B] Phosphorus, due to the presence of ' $d$ ' orbital
[C] Arsenic and Antimony, because they possess ' $f$ ' orbital
[D] Bismuth, because of the stabilization of 6s orbital and inert-pair effect induced by relativistic effect.
63. Calculate the potential and equilibrium constant of the following cell in the direction of the spontaneous reaction

$$
\mathrm{Pt}, \mathrm{H}_{2}(0.9 \mathrm{~atm})\left|\mathrm{H}^{+}(0.1 \mathrm{M})\right||\mathrm{KCl}(0.1 \mathrm{M}), \mathrm{AgCl}| \mathrm{Ag}
$$

Given: $E_{\mathrm{Ag}^{+} / \mathrm{AgCl}}^{\circ}=+0.22 \mathrm{~V} ; E_{2 \mathrm{H}^{+} / \mathrm{H} 2}^{\circ}=0.0 \mathrm{~V}$
[A] +0.22 V and $2.9 \times 10^{7}$
[B] +0.22 V and 7.46
[C] +0.33 V and $2.9 \times 10^{7}$
[D] +0.34 V and 7.46
64. The number of bridging CO in $\left[\mathrm{Os}_{4}(\mathrm{CO})_{16}\right]$ is/are
[A] 0
[B] 1
[C] 2
[D] 3
65. The hapticity of the cycloheptatriene in $\left(\eta^{n}-\mathrm{C}_{7} \mathrm{H}_{8}\right)_{2} \mathrm{Cr}(\mathrm{CO})_{3}$, and $\left(\eta^{n}-\mathrm{C}_{7} \mathrm{H}_{8}\right)_{2} \mathrm{Fe}(\mathrm{CO})_{3}$ compounds is
[A] 4 and 6, respectively
[B] 4 and 4, respectively
[C] 5 and 6 , respectively
[D] 6 and 4, respectively
66. Which statements among the following are true for Hemocyanin?
(i) Blue blood
(ii) It transports $\mathrm{O}_{2}$
(iii) The oxygen has oxo coordination mode
(iv) Involves MLCT transition during $\mathrm{O}_{2}$ binding
[A] (i) and (ii)
[B] (i), (iii) and (iv)
[C] (ii) and (iii)
[D] (i) and (iv)
67. Photosystem II in photosynthesis contains
[A] tetranuclear magnesium cluster as the catalytic site and catalyses the reduction of water.
[B] tetranuclear manganese cluster as the catalytic site and catalyses the oxidation of water.
[C] tetranuclear iron cluster as the catalytic site and catalyses the reduction of $\mathrm{CO}_{2}$.
[D] tetranuclear cobalt cluster as the catalytic site and catalyses the oxidation of glucose.
68. If $B H$ is isolobal with $\left[M\left(\eta^{5}-C_{5} H_{5}\right)\right]$, then $M$ is
[A] Co
[B] Mn
[C] Fe
[D] Cr
69. The coordination geometry of the metal center and the $\mathrm{Co}-\mathrm{N}-\mathrm{O}$ bond angle in $\left[\mathrm{Co}(\mathrm{CO})_{3}(\mathrm{NO})\right]$ are, respectively
[A] tetrahedral and $120^{\circ}$
[B] square-planar and $180^{\circ}$
[C] tetrahedral and $180^{\circ}$
[D] square-planar and $120^{\circ}$
70. The relationship between the crystal field splitting in a cubic geometry $\left(\Delta_{c}\right)$ an that in an octahedral geometry $\left(\Delta_{0}\right)$ is
[A] $\Delta_{c}=4 / 3 \Delta_{0}$
[B] $\quad \Delta_{\mathrm{c}}=4 / 9 \Delta_{\mathrm{o}}$
[C] $\Delta_{c}=8 / 6 \Delta_{0}$
[D] $\Delta_{c}=8 / 9 \Delta_{0}$
71. The basic structural unit of infinite single chain silicate, infinite double chain silicate, and layered structure of silicate are, respectively
[A] $\left[\mathrm{Si}_{4} \mathrm{O}_{11}\right]_{\mathrm{n}}{ }^{6 \mathrm{n}-},\left[\mathrm{SiO}_{3}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-}$, and $\left[\mathrm{Si}_{2} \mathrm{O}_{5}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-}$
[B] $\left[\mathrm{SiO}_{3}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-},\left[\mathrm{Si}_{2} \mathrm{O}_{5}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-}$, and $\left[\mathrm{Si}_{4} \mathrm{O}_{11}\right]_{\mathrm{n}}^{6 \mathrm{n}-}$
[C] $\left[\mathrm{SiO}_{3}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-},\left[\mathrm{Si}_{6} \mathrm{O}_{18}\right]^{12-}$, and $\left[\mathrm{Si}_{2} \mathrm{O}_{5}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-}$
[D] $\left[\mathrm{SiO}_{3}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-},\left[\mathrm{Si}_{4} \mathrm{O}_{11}\right]_{\mathrm{n}}{ }^{6 \mathrm{n}-}$, and $\left[\mathrm{Si}_{2} \mathrm{O}_{5}\right]_{\mathrm{n}}{ }^{2 \mathrm{n}-}$
72. Choose the correct statement regarding the mechanism of the following two reactions
(i) $\quad \mathrm{W}(\mathrm{CO})_{6}+\mathrm{PPh}_{3} \rightarrow \mathrm{~W}(\mathrm{CO})_{5}\left(\mathrm{PPh}_{3}\right)+\mathrm{CO}$
(ii) $\quad\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}+{ }^{14} \mathrm{CN}^{-} \rightarrow\left(\mathrm{Ni}(\mathrm{CN})_{3}\left({ }^{14} \mathrm{CN}\right)\right]^{2-}+\mathrm{CN}^{-}$
[A] (i) is associative while (ii) is dissociative
[B] (i) is dissociative while (ii) is associative
[C] Both (i) and (ii) are associative
[D] Both (i) and (ii) are dissociative
73. How many valence shell electron pairs are present in $\mathrm{BrF}_{5}, \mathrm{ICl}_{4}^{-}$and $\mathrm{XeF}_{4}$ ?
[A] 6,5 and 6 .
[B] 6,4 and 4 .
[C] 6,6 , and 6 .
[D] 5, 4 and 4 .
74. In substitution reaction of a ligand in square planar complex
[A] Trans complex leads to cis complex and cis complex leads to trans complex.
[B] Trans complex leads to cis complex and cis complex also leads to cis complex.
[C] Trans complex leads to trans complex and cis complex also leads to trans complex
[D] Trans complex leads to trans complex and cis complex leads to cis complex.
75. . In a nuclear decay series, ${ }^{238} U_{92}$ nucleus first decays an $\alpha$-particle followed by two $\beta$ particles and two $\alpha$-particles in consecutive four steps. The resulting nucleus will be
[A] ${ }^{222} \mathrm{Rn}_{86}$
[B] $\quad{ }^{226} \mathrm{Ra}_{88}$
[C] $\quad{ }^{214} \mathrm{~Pb}_{82}$
[D] $\quad{ }^{230} \mathrm{Th}_{90}$
76. The number of observed versus predicted isomers for three different geometries (hexagonal, trigonal, and octahedral) of coordination complex $\mathrm{MA}_{3} \mathrm{~B}_{3}$.
[A] 2 and $3,3,2$
[B] 3 and $3,3,2$
[C] 2 and $2,3,2$
[D] 4 and $3,3,2$
77. Select the accurate statement from the options provided.
[A] Complexes of $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{II})$ are usually four coordinate, trigonal pyramidal and diamagnetic in nature.
[B] Complexes of $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{II})$ are usually four coordinate, tetrahedral and diamagnetic in nature.
[C] Complexes of $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{II})$ are usually four coordinate, square planar and paramagnetic in nature.
[D] Complexes of $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{II})$ are usually four coordinate, square planar and diamagnetic in nature.
78. Predict the ${ }^{31} \mathrm{P}$ NMR spectrum of $\mathrm{P}\left(\mathrm{OCH}_{3}\right)_{3}$ considering that ${ }^{3} \mathrm{~J}_{\mathrm{PH}}$ coupling is observed in the compound. $\left[I=1 / 2\right.$ for ${ }^{31} \mathrm{P}$ and $\left.{ }^{1} \mathrm{H}\right]$
[A] 10 line pattern
[B] 9 line pattern
[C] 6 line pattern
[D] 12 line pattern
79. Using the Wade's rules, predict total valence electron count, skeleton electron pair, and type of structure for $\left[\mathrm{B}_{5} \mathrm{H}_{11}\right]$.
[A] 26, 8, and arachno
[B] 26, 13, and ido
[C] 26, 13, and arachno
[D] 26, 7, and ido
80. Select the wrong statement of graphite from the options provided.
[A] The graphene planes are separated from each other with distance of $\sim 3.35 \AA$.
[B] The readily cleavage of graphite parallel to the planes of atoms is largely due to the presence of impurities as well as weak attraction between the layers.
[C] The electrical conductivity of graphite is closely related to the structure of its delocalized $\pi$ bonds.
[D] Its electrical conductivity perpendicular to the planes is high and decrease with increasing temperature.

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\text { Answer Key - Ph. D. Chemistry - } 2021 \text { (January) }
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