21. The correct order of basicity for the following anions is

(I) \(\text{O}^\text{\scriptsize \text{\textbullet}}\text{NO}_2\)  
(II) \(\text{O}^\text{\scriptsize \text{\textbullet}}\text{NO}_2\)  
(III) \(\text{O}^\text{\scriptsize \text{\textbullet}}\text{NO}_2\)

(a) II > III > I  (b) I > II > III  (c) II > I > III  (d) III > II > I

22. The major product formed in the reaction of 2, 5-hexanedione with \(\text{P}_2\text{O}_5\) is

(a)  
(b)  
(c)  
(d)  

23. The absolute configuration of the two stereogenic (chiral) centres in the following molecule is

(a) 5R, 6R  (b) 5R, 6S  (c) 5S 6R  (d) 5S, 6S

24. The correct statement about the following molecule is

(a) Molecular is chiral and possesses a chiral plane  
(b) Molecule is chiral and possesses a chiral axis.  
(c) Molecule is achiral as it possesses a plane of symmetry.  
(d) Molecule is achiral as it possesses a centre of symmetry.

25. Consider the following statements about cis- and trans-decalins
(A) cis-isomer is more stable than trans-isomer  
(B) trans-isomer is more stable than cis-isomer  
(C) trans-isomer undergoes ring-flip  
(D) cis-isomer undergoes ring-flip 

The correct statements among the above are
(a) B and D  (b) A and C  (c) A and D  (d) B and C
26. In bis(dimethylglyoximato)nickel(II), the number of Ni–N, Ni–O and intramolecular hydrogen bond(s), respectively are
   (a) 4, 0 and 2  
   (b) 2, 2 and 2  
   (c) 2, 2 and 0  
   (d) 4, 0 and 1

27. Among the following species, (A) Ni(II) as dimethylglyoximate, (B) Al(III) as oximate, (C) Ag(I) as chloride, those that precipitate with the urea hydrolysis method are
   (a) A, B and C  
   (b) A and B  
   (c) A and C  
   (d) B and C

28. If an enzyme fixes N\textsubscript{2} in plants by evolving H\textsubscript{2}, the number of electrons and protons associated with that, respectively are
   (a) 6 and 6  
   (b) 8 and 8  
   (c) 6 and 8  
   (d) 8 and 6

29. The particles postulated to always accompany the positron emission among
   (A) neutrino,  
   (B) anti-neutrino, (C) electron, are
   (a) A, B and C  
   (b) A and B  
   (c) A and C  
   (d) B and C

30. Toxicity of cadmium and mercury in the body is being reversed by proteins, mainly using the amino acid residue,
   (a) Glycine  
   (b) Leucine  
   (c) Lysine  
   (d) Cysteine

31. NiBr\textsubscript{2} reacts with (Et)(Ph\textsubscript{2})P at –78ºC in CS\textsubscript{2} to give red compound ‘A’, which upon standing at room temperature turns green to give compound, ‘B’ of the same formula. The measured magnetic moments of ‘A’ and ‘B’ are 0.0 and 3.2 BM, respectively. The geometries of ‘A’ and ‘B’ are
   (a) square planar and tetrahedral  
   (b) tetrahedral and square planar  
   (c) square planar and octahedral  
   (d) tetrahedral and octahedral

32. The correct non-linear and iso-structural pair is
   (a) SCl\textsubscript{2} and I\textsubscript{3}–  
   (b) SCl\textsubscript{2} and I\textsubscript{3}+  
   (c) SCl\textsubscript{2} and ClF\textsubscript{2}–  
   (d) I\textsubscript{3}+ and ClF\textsubscript{2}–

33. Ozone present in upper atmosphere protects people on the earth
   (a) due to its diamagnetic nature  
   (b) due to its blue colour  
   (c) due to absorption of radiation of wavelength at 255nm  
   (d) by destroying chlorofluoro carbons

34. If L is a neutral monodentate ligand, the species, [AgL\textsubscript{4}]\textsuperscript{2+}, [AgL\textsubscript{6}]\textsuperscript{2+} and [AgL\textsubscript{4}]\textsuperscript{3+}, respectively are
   (a) paramagnetic, paramagnetic and dimagnetic  
   (b) paramagnetic, diamagnetic and paramagnetic  
   (c) diamagnetic, paramagnetic and diamagnetic  
   (d) paramagnetic, diamagnetic and diamagnetic

35. Chromite ore on fusion with sodium carbonate gives
   (a) Na\textsubscript{2}CrO\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3}  
   (b) Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} and Fe\textsubscript{2}O\textsubscript{3}  
   (c) Cr\textsubscript{2}(CO\textsubscript{3})\textsubscript{3} and Fe(OH)\textsubscript{3}  
   (d) Na\textsubscript{2}CrO\textsubscript{4} and Fe(\textsubscript{2}CO\textsubscript{3})\textsubscript{3}

36. The ligand(s) that is (are) fluxional in \(\left[\left(\eta^5 - C_5H_5\right)\left(\eta^1 - C_5H_5\right)\text{Fe}(\text{CO})_2\right]\) in the temperature range 221–298K, is (are)
   (a) \(\eta^5 - C_5H_5\)  
   (b) \(\eta^1 - C_5H_5\)  
   (c) \(\eta^5 - C_5H_5\) and CO  
   (d) \(\eta^1 - C_5H_5\) and CO

37. \([\text{CoL}_6]\textsuperscript{3} \) is red in colour whereas \([\text{CoL’}_6]\textsuperscript{3+} \) is green. L and L’ respectively corresponds to,
   (a) NH\textsubscript{3} and H\textsubscript{2}O  
   (b) NH\textsubscript{3} and 1, 10-phenanthroline  
   (c) NH\textsubscript{3} and 1, 10-phenanthroline  
   (d) H\textsubscript{2}O and NH\textsubscript{3}

38. The oxidation state of Ni and the number of metal-metal bonds in \([\text{Ni}_2(\text{CO})_6]\textsuperscript{2-} \) that are consistent with the 18 electron rule are
   (a) Ni(–II), 1 bond  
   (b) Ni(IV), 2 bonds  
   (c) Ni(–I), 1 bond  
   (d) Ni(IV), 3 bonds
39. Structures of $\text{SbPh}_5$ and $\text{PPh}_5$ respectively are
   (a) trigonal bipyramidal, square pyramidal
   (b) square pyramidal, trigonal bipyramidal
   (c) trigonal bipyramidal, trigonal bipyramidal
   (d) square pyramidal, square pyramidal

40. The typical electronic configurations of the transition metal centre for oxidative addition
   (a) $d^0$ and $d^8$
   (b) $d^6$ and $d^8$
   (c) $d^8$ and $d^{10}$
   (d) $d^5$ and $d^{10}$

41. Gelatin added during the polarographic measurement carried out using dropping mercury electrode
   (a) reduces streaming motion of Hg drop
   (b) decreases viscosity of the solution
   (c) eliminates migrating current
   (d) prevents oxidation of Hg

42. The $pK_a$ values of the following salt of aspartic acid are indicated below. The predominant species
   that would exist at pH = 5 is
   
   \[
   \text{H}_3\text{N}\text{COOH} \quad (pK_a = 9.9) \quad \text{H}_3\text{N}\text{COOH} \quad (pK_a = 2.0) \quad \text{H}_3\text{N}\text{COOH} \quad (pK_a = 3.9) \quad \text{H}_3\text{N}\text{COOH}
   \]

43. The major product formed in the following photochemical reaction is

44. The pair of solvents in which $\text{PCl}_5$ does NOT ionize, is
   (a) $\text{CH}_3\text{CN}, \text{CH}_3\text{NO}_2$
   (b) $\text{CH}_3\text{CN}, \text{CCl}_4$
   (c) $\text{C}_6\text{H}_6, \text{CCl}_4$
   (d) $\text{CH}_2\text{CN}, \text{C}_6\text{H}_6$

45. The major product formed in the following reaction is
46. The correct order for the rates of electrophilic aromatic substitution of the following compound is

\[
\begin{align*}
(\text{I}) & \quad (\text{II}) & \quad (\text{III}) \\
\text{Cl} & \quad \text{Me} & \quad \text{Me}
\end{align*}
\]

(a) I > II > III (b) II > I > III (c) III > II > I (d) I > III > II

47. The commutator of the kinetic energy operator, \( \hat{T}_x \) and the momentum operator, \( \hat{p}_x \) for the one-dimensional case is

(a) \( i\hbar \) (b) \( i\hbar \frac{d}{dx} \) (c) 0 (d) \( i\hbar x \)

48. The major product formed in the reaction of trans-1-bromo-3-methylcyclobutane with sodium iodide in DMF is

(a) \( \text{Me} \) (b) \( \text{Me} \) (c) \( \text{Me} \) (d) \( \text{Me} \)

49. When Si is doped with a Group V element,
(a) donor levels are created close to the valence band
(b) donor levels are created close to the conduction band
(c) acceptor levels are created close to the valence band
(d) acceptor levels are created close to the conduction band

50. The symmetry point group of propyne is

(a) \( C_3 \) (b) \( C_{3v} \) (c) \( D_3 \) (d) \( D_{3d} \)

51. For a first order reaction \( A \rightarrow \text{products} \), the plot of \( \ln \left( \frac{[A]_t}{[A]_0} \right) \) vs time, where \([A]_0\) and \([A]_t\) refer to concentration at time \( t = 0 \) and \( t \) respectively, is

(a) a straight line with a positive slope passing through origin
(b) a straight line with a negative slope passing through origin
(c) an exponential curve asymptotic to the time axis
(d) a curve asymptotic to the \( \ln \left( \frac{[A]_t}{[A]_0} \right) \) axis.

52. In radical chain polymerization, the quantity given by the rate of monomer depletion, divided by the rate of propagating radical formation is called

(a) kinetic chain length (b) propagation efficiency
(c) propagation rate constant (d) polymerization time

53. Number of rotational symmetry axes for triclinic crystal system is

(a) 4 (b) 3 (c) 1 (d) 0

54. Generally, hydrophobic colloids are flocculated efficiently by ions of opposite type and high charge number. This is consistent with the

(a) peptization principle (b) krafft theory
(c) Hardy-Schulze rule (d) Langmuir adsorption mechanism
55. Examine the following first order consecutive reactions. The rate constant (in s\(^{-1}\) units) for each step is given above the arrow mark.

(A) \( P \xrightarrow{10^3} Q \xrightarrow{10^6} R \)  
(B) \( P \xrightarrow{10^5} Q \xrightarrow{10^3} R \)  
(C) \( P \xrightarrow{10^7} Q \xrightarrow{10^7} R \)  
(D) \( P \xrightarrow{10^2} Q \xrightarrow{10^6} R \)

Steady-state approximation can be applied to
(a) A only  
(b) C only  
(c) B and C only  
(d) A and D only

56. The figure below represents the path followed by a gas during expansion from \( A \rightarrow B \). The work done is (L atm)

- (a) 0  
- (b) 9  
- (c) 5  
- (d) 4

57. An aqueous solution of an optically pure compound of concentration 100 mg in 1 mL of water and measured in a quartz tube of 5 cm length was found to be \(-3^\circ\). The specific rotation is
(a) \(-30^\circ\)  
(b) \(-60^\circ\)  
(c) \(-6^\circ\)  
(d) \(+6^\circ\)

58. Two phases (\( \alpha \) and \( \beta \)) of a species are in equilibrium. The correct relations observed among the variables, \( T, p \) and \( \mu \) are
(a) \( T_\alpha = T_\beta, p_\alpha \neq p_\beta, \mu_\alpha = \mu_\beta \)  
(b) \( T_\alpha \neq T_\beta, p_\alpha = p_\beta, \mu_\alpha = \mu_\beta \)  
(c) \( T_\alpha = T_\beta, p_\alpha = p_\beta, \mu_\alpha = \mu_\beta \)  
(d) \( T_\alpha = T_\beta, p_\alpha = p_\beta, \mu_\alpha \neq \mu_\beta \)

59. The number of configurations in the most probable state, according to Boltzmann formula, is
(a) \( e^{S/k_B} \)  
(b) \( e^{-S/k_B} \)  
(c) \( e^{-E/k_B T} \)  
(d) \( e^{-\Delta G/k_B T} \)

60. The correct match of the \(^1\)H NMR chemical shifts (\( \delta \)) of the following species/compounds is

- (a) I : 5.4; II : 7.2; III : 9.2  
- (b) I : 9.2; II : 7.2; III : 5.4  
- (c) I : 9.2; II : 5.4; III : 7.2  
- (d) I : 7.2; II : 9.2; III : 5.4

61. The major products formed in the following are

- (a) \( \text{Ac} \xrightarrow{(i) \text{Ph}_3\text{C}^- \text{Na}^+} \text{Ph}_3\text{C}^- \xrightarrow{(ii) \text{H}_3\text{O}^+} \text{OH} + \text{Ph}_3\text{C}^-\text{CH}_2\text{CH}_3 \)  
- (b) \( \text{HO} \xrightarrow{\text{CPh}_3} \text{OH} + \text{EtOH} \)  
- (c) \( \text{CO} \xrightarrow{\text{OEt}} \text{CO} + \text{EtOH} \)  
- (d) \( \text{HO} \xrightarrow{\text{CPh}_3} \text{OH} + \text{H}_2\text{C}^-\text{CH}_2 \)
62. In a Diels-Alder reaction, the most reactive diene amongst the following is
   (a) (4E)-1, 4-hexadiene   (b) (4Z)-1, 4-hexadiene
   (c) (2E, 4E)-2, 4-hexadiene  (d) (2Z, 4Z)-2, 4-hexadiene

63. Consider the statements about the following structures X and Y

   \[
   \begin{align*}
   X & : \text{Ph-CN} \\
   Y & : \text{Ph-NH} 
   \end{align*}
   \]

   (A) X and Y are resonance structures  (B) X and Y are tautomers
   (C) Y is more basic than X  (D) X is more basic than Y

   The correct statement(s) among the above is/are
   (a) A and C  (b) C  (c) B and D  (d) B and C

64. Pericyclic reaction involved in one of the steps of the following reaction sequence is

   \[
   \begin{align*}
   \ce{C(S)_2} & \xrightarrow{(i) \text{heat}} \ce{C(S)} \xrightarrow{(ii) \text{EtO}_3P} \ce{C(O)} \\
   \text{Ph} & \quad \text{Ph} 
   \end{align*}
   \]

   (a) [1, 3] sigmatropic shift  (b) [3, 3] sigmatropic shift
   (c) [1, 5] sigmatropic shift  (d) [2, 3] sigmatropic shift

65. Atorvastatin (structure given below) is a

   \[
   \begin{align*}
   &\text{HOOC} \\
   &\text{Me} \\
   &\text{Me} \\
   &\text{PhH} \\
   &\text{Ph} \\
   &\text{Ph} \\
   &\text{F} \\
   &\text{OH} \\
   &\text{OH} \\
   &\text{O} \\
   &\text{O} \\
   \end{align*}
   \]

   (a) cholesterol lowering drug  (b) blood sugar lowering drug
   (c) anti-plasmodial drug  (d) anti-HIV drug

66. The maximum bond order obtained from the molecular orbitals of a transition metal dimer, formed as linear combinations of d-orbitals alone, is

   (a) 3  (b) 4  (c) 5  (d) 6

67. The term symbol that is NOT allowed for the np\(^+\) configuration is

   (a) \(^1D\)  (b) \(^3P\)  (c) \(^1S\)  (d) \(^3D\)

68. If the ionization energy of H atom is \(x\), the ionization energy of Li\(^{2+}\), is

   (a) 2\(x\)  (b) 3\(x\)  (c) 9\(x\)  (d) 27\(x\)

69. If temperature is doubled and the mass of the gaseous molecule is halved, the rms speed of the molecular will change by a factor of

   (a) 1  (b) 2  (c) 1/2  (d) 1/4

70. In the graph below, the correct option, according to Kohlrausch law, is

   \[
   \begin{align*}
   &\text{A} \\
   &\text{B} \\
   &\text{C} \\
   &\text{D} \\
   &\text{J} \rightarrow 
   \end{align*}
   \]

   (a) A is a weak electrolyte and B is a strong electrolyte
   (b) A is a strong electrolyte and B is a weak electrolyte
   (c) C is a strong electrolyte and D is a weak electrolyte
   (d) C is weak electrolyte and D is a strong electrolyte
PART-C

71. Reaction of \([\text{Ru(NH}_3\text{)}_5\text{(isonicotinamide)}]^3+\) with \([\text{Cr(H}_2\text{O)}_6]^3+\) occurs by inner sphere mechanism and rate of the reaction is determined by dissociation of the successor complex. It is due to the
(a) Inert ruthenium bridged to inert chromium centre
(b) Inert ruthenium bridged to labile chromium centre
(c) Labile ruthenium bridged to inert chromium centre
(d) Labile ruthenium bridged to labile chromium centre

72. Consider the second order rate constants for the following outer-sphere electron transfer reactions:

\[
\frac{[\text{Fe(H}_2\text{O)}_6]^3+}{[\text{Fe(H}_2\text{O)}_6]^2+} = 4.0 \text{ M}^{-1} \text{ sec}^{-1}
\]
\[
\frac{[\text{Fe(phen)}_3]^3+}{[\text{Fe(phen)}_3]^2+} = 3.0 \times 10^7 \text{ M}^{-1}
\]
(phen = 1, 10-phenanthroline)
The enhanced rate constant for the second reaction is due to the fact that
(a) The 'phen' is a \(\pi\)-acceptor ligand that allows mixing of electron donor and acceptor orbitals that enhances the rate of electron transfer
(b) The 'phen' is a \(\pi\)-donor ligand that enhances the rate of electron transfer
(c) The 'phen' forms charge transfer complex with iron and facilitates the electron transfer
(d) The 'phen' forms kinetically labile complex with iron and facilitates the electron transfer.

73. The compound \([\text{Re}_2(\text{Me}_2\text{PPh})_4\text{Cl}_4] (M)\) having a configuration of \(\sigma^2\pi^4\delta^2\delta'^2\) can be oxidized to \(M^{+}\) and \(M^{2+}\). The formal metal-metal order in \(M, M^{+}\) and \(M^{2+}\) respectively, are
(a) 3.0, 3.5 and 4.0 (b) 3.5, 4.0 and 3.0 (c) 4.0, 3.5 and 3.0 (d) 3.0, 4.0 and 3.5

74. In low chloride ion concentration, the anticancer drug cis-platin hydrolyses to give a diaqua complex and this binds to DNA via adjacent guanine

![guanine](guanine.png)
The coordinating atom of guanine to Pt(II) is
(a) N1 (b) N3 (c) N7 (d) N9

75. The \(^{19}\text{F} \text{NMR spectrum of ClF}_3\) shows
(a) doublet and triplet for a T-shaped structure
(b) singlet for a trigonal planar structure
(c) singlet for a trigonal pyramidal structure
(d) doublet and singlet for a T-shaped structure

76. The low temperature (–98ºC) \(^{19}\text{F} \text{NMR spectrum of SF}_4\) shows doublet of triplets. It is consistent with the point group symmetry.
(a) \(C_{3v}\) (b) \(C_{4v}\) (c) \(T_d\) (d) \(C_{2v}\)

77. Amongst organolithium (A), Grignard (B) and organoaluminium (C) compounds, those react with \(\text{SiCl}_4\) to give compound containing Si-C bond are
(a) A and B (b) B and C (c) A and C (d) A, B and C
78. In its electronic spectrum, \( [\text{V(H}_2\text{O)}_6]^{3+} \) exhibits two absorption bands, one at 17,800 \( (v_1) \) and the second at 25,700 \( (v_2) \) cm\(^{-1}\). The correct assignment of these bands, respectively, is

(a) \( v_1 = ^3T_{1g} (F) \rightarrow ^3T_{2g} (F) \), \( v_2 = ^3T_{1g} (F) \rightarrow ^3T_{1g} (P) \)

(b) \( v_1 = ^3T_{1g} (F) \rightarrow ^3T_{1g} (P) \), \( v_2 = ^3T_{1g} (F) \rightarrow ^3T_{2g} (P) \)

(c) \( v_1 = ^3A_{2g} \rightarrow ^3T_{1g} (F) \), \( v_2 = ^3A_{2g} \rightarrow ^3T_{2g} (F) \)

(d) \( v_1 = ^3A_{2g} \rightarrow ^3T_{2g} (F) \), \( v_2 = ^3A_{2g} \rightarrow ^3T_{1g} (F) \)

79. Reactions of elemental arsenic with hot and conc. \( \text{HNO}_3 \) and \( \text{H}_2\text{SO}_4 \), respectively, give

(a) \( \text{As}_2\text{O}_6 \) and \( \text{As}_2(\text{SO}_4)_3 \)

(b) \( \text{As(NO}_3)_5 \) and \( \text{As}_2(\text{SO}_4)_3 \)

(c) \( \text{As}_4\text{O}_6 \) and \( \text{H}_3\text{AsO}_4 \)

(d) \( \text{H}_3\text{AsO}_4 \) and \( \text{As}_2\text{O}_6 \)

80. The total valence electron count and the structure type adopted by the complex \([\text{Fe}_5(\text{CO})_{15}C]\) respectively, are

(a) 74 and nido

(b) 60 and closo

(c) 84 and arachno

(d) 62 and nido

81. \(^1\text{H} \text{NMR} \) spectrum of \( [\eta^5-C_5\text{H}_5\text{Rh})(\text{C}_2\text{H}_4)_{1/2}] \) at \(-20^\circ\text{C}\) shows a typical AA’ XX’ pattern in the olefinic region. On increasing the temperature to \~70^\circ\text{C}\), the separate lines collapse into a single line which is due to

(a) free rotation of the ethylene ligand about the metal-olefin bond

(b) intermolecular exchange between the ethylene ligands

(c) intermolecular exchange between the ethylene ligands

(d) change in hapticity of the cyclopentadienyl ligand

82. The nuclides among the following, capable of undergoing fission by thermal neutrons, are

(A) \( ^{233}\text{U} \)

(B) \( ^{235}\text{U} \)

(C) \( ^{239}\text{Pu} \)

(D) \( ^{232}\text{Th} \)

(a) A, B and D

(b) A, C and D

(c) B, C and D

(d) A, B and C

83. The use of dynamic inert atmosphere in thermogravimetric analysis (TGA) is

(a) decreases decomposition temperature

(b) decreases rate of decomposition

(c) reduces rate of decomposition

(d) increases weight loss

84. The correct statements for hollow cathode lamp (HCL) from the following are

(A) HCL is suitable for atomic absorption spectroscopy (AAS)

(B) lines emitted from HCL are very narrow

(C) the hardening of lamp makes it unsuitable for AAS

(D) transition elements used in lamps have short life

(a) A, B and C

(b) B, C and D

(c) C, D and A

(d) D, A and B

85. Identify the correct statement about \( [\text{Ni}(\text{H}_2\text{O})_6]^{2+} \) and \( [\text{Cu}(\text{H}_2\text{O})_6]^{2+} \)

(a) All Ni-O and Cu-O bond lengths of individual species are equal

(b) Ni-O(equatorial) and Cu-O(equatorial)

(c) All Ni-O bond lengths are equal whereas Cu-O (equatorial) bonds are shorter than Cu-O(axial) bonds

(d) All Cu-O bond lengths are equal whereas Ni-O(equatorial) bonds are shorter than Ni-O(axial) bonds.

86. Reaction of nitrosyl tetrafluoroborate to Vaska’s complex gives complex A with \( \angle M-N-O = 124^\circ \). The complex A and its N-O stretching frequency are, respectively

(a) \([\text{IrCl(CO)(NO)(PPh}_3)_2]\text{BF}_4, 1620 \text{ cm}^{-1}\)

(b) \([\text{IrCl(CO)(NO)(PPh}_3)_2](\text{BF}_4)_2, 1730 \text{ cm}^{-1}\)

(c) \([\text{IrCl(CO)(NO)(PPh}_3)_2](\text{BF}_4)_3, 1520 \text{ cm}^{-1}\)

(d) \([\text{IrCl(CO)(NO)(PPh}_3)_2], 1820 \text{ cm}^{-1}\)
87. The correct order of decreasing electronegativity of the following atoms is,
(a) As > Al > Ca > S  (b) S > As > Al > Ca  (c) Al > Ca > S > As  (d) S > Ca > As > Al

88. A 1 : 2 mixture of Me_{2}NCH_{2}CH_{2}PPh_{2} and KSCN with K_{2}[PdCl_{4}] gives a square planar complex A. Identify the correct pairs of donor atoms trans to each other in complex A from the following combinations.
(a) P, N  (b) N, S  (c) P, S  (d) N, N

89. For a low energy nuclear reaction, ^{24}\text{Mg}(d, \alpha)^{22}\text{Na}, the correct statements from the following are
(A) Kinetic energy of d particle is not fully available for exciting ^{24}\text{Mg}.
(B) Total number of protons and neutrons is conserved.
(C) Q value of nuclear reaction is much higher in magnitude relative to heat of chemical reaction.
(D) Threshold energy is \leq Q value.
(a) A, B and C  (b) A, B and D  (c) B, C and D  (d) A, C and D

90. At pH 7, the zinc(II) ion in carbonic anhydrase reacts with CO_{2} to give
(a) Zn-O-H
(b) Zn-O-C
(c) Zn-O-C
(d) Zn-O-C

91. Molybdoenzymes can both oxidize as well as reduce the substrates, because
(a) Mo(VI) is more stable than Mo(IV)
(b) Mo(IV) can transfer oxygen atom to the substrate and Mo(VI) can abstract oxygen atom from the substrate.
(c) Conversion of Mo(VI) to Mo(IV) is not favoured
(d) Mo(VI) can transfer oxygen atom to the substrate and Mo(IV) can abstract oxygen atom from the substrate.

92. A comparison of the valence electron configuration of the elements, Sm and Eu suggests that
(a) Sm is a better one electron reductant than Eu
(b) Sm is a better one electron oxidant than Eu
(c) Facile oxidation state is +2 for both the elements
(d) Both of these display similar redox behaviour.

93. The cooperative binding of O_{2} in hemoglobin is due to
(a) a decrease in size of iron followed by changes in the protein conformation
(b) an increase in size of iron followed by changes in the protein conformation
(c) a decrease in size of iron that is NOT accompanied by the protein conformational changes
(d) an increase in size of iron that is NOT accompanied by the protein conformational changes.

94. Amongst the following which is not isolobal pairs
(a) Mn(CO)_{5}, CH_{3}  (b) Fe(CO)_{4}, O  (c) Co(CO)_{3}, R_{2}Si  (d) Mn(CO)_{3}, RS

95. The correct order of the size of S, S^{2-}, S^{2+} and S^{4+} species is,
(a) S > S^{2+} > S^{4+} > S^{2-}  (b) S^{2+} > S^{4+} > S^{2-} > S
(c) S^{2-} > S > S^{2+} > S^{4+}  (d) S^{4+} > S^{2-} > S > S^{2+}
96. The major product formed in the following reaction is

\[
\text{BrHn} \rightarrow \text{Bu}_3\text{SnH, AIBN benzene reflux}
\]

(a) \hspace{1cm} (b) \hspace{1cm} (c) \hspace{1cm} (d)

97. The correct combination of reagents to effect the following conversion is

(a) (i) \text{Ph,P\textsuperscript{+}CH\_2OMeCl, BuLi, (ii) H\_2O\_2, Jones’ reagent}
(b) (i) \text{H\_2N NH\_Ts; (ii) BuLi (2 equiv); (iii) DMF}
(c) (i) \text{H\_2N NH\_Ts; (ii) BuLi (2 equiv); (iii) CO\_2}
(d) (i) \text{ClCH\_2CO\_2Et, LDA; (ii) BF\_3.OEt\_2; (iii) DMSO, (COCl\_2, Et\_3N, \text{–78ºC to rt.}}

98. The major product formed in the following reaction is

\[
\text{Bu}_3\text{N}^+\text{Br}^- \rightarrow \text{anhyd. CF}_3\text{COOH CH}_2\text{Cl}_2
\]

(a) \hspace{1cm} (b) \hspace{1cm} (c) \hspace{1cm} (d)

99. Consider the following reaction,

\[
\text{O} + \text{Ph–N}_3 \rightarrow \text{CF}_3\text{COOH}
\]

The appropriate intermediate involved in this reaction is

(a) \hspace{1cm} (b) \hspace{1cm} (c) \hspace{1cm} (d)
100. The correct \( ^{13} \text{C} \) NMR chemical (\( \delta \)) shift values of carbons labeled a-e in the following ester are

(a) a : 19; b : 143; c : 167; d : 125; e : 52  
(b) a : 52; b : 143; c : 167; d : 125; e : 19  
(c) a : 52; b : 167; c : 143; d : 125; e : 19  
(d) a : 52; b : 167; c : 125; d : 143; e : 19

101. The products A and B in the following reaction sequence are

\[
\text{PhCOOH} \xrightarrow{\text{MeOCl}} (A) \xrightarrow{\text{Et}_3\text{N}} (B)
\]

(a) A : \[
\text{PhCOO} \xrightarrow{\text{MeO}} \text{Me}
\]
B : \[
\text{PhCONH}
\]
(b) A : \[
\text{PhCOCl}
\]
B : \[
\text{PhCONH}
\]
(c) A : \[
\text{PhCOO} \xrightarrow{\text{MeO}} \text{Me}
\]
B : \[
\text{MeO} \xrightarrow{\text{N}} \text{PhCONH}
\]
(d) A : \[
\text{PhCOCl}
\]
B : \[
\text{PhCO}
\]

102. The biosynthesis of isopentenyl pyrophosphate from acetyl CoA involves:
A. Four molecules of acetyl CoA  
B. Three molecules of ATP  
C. Two molecules of NADPH  
D. Two molecules of lipoic acid  
The correct options among these are
(a) A, B and D  
(b) A and B  
(c) B and C  
(d) A, C and D

103. Amongst the following, the major products formed in the following photochemical reactions are

\[
\text{CH}_2=\text{CHCH} = \text{CH} \xrightarrow{h_\nu} \text{HO}
\]

A  B  C  D

(a) A and C  
(b) B and C  
(c) A and D  
(d) A and B
104. The products A and B in the following reaction sequence are

\[
\begin{align*}
\text{BnO} & \quad \text{OMe} \\
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{MeO} & \quad \text{H}_2\text{N} \\
\text{MeO} & \quad \text{H}_2\text{N} \\
\end{align*}
\]

\[\text{heat} \rightarrow \text{B} \]

\[\text{A:} \quad \text{B:} \]

(a) A: \hspace{1cm} (b) A: \hspace{1cm} (c) A: \hspace{1cm} (d) A:

\[\begin{align*}
\text{BnO} & \quad \text{OMe} \\
\text{BnO} & \quad \text{OMe} \\
\text{BnO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{MeO} \\
\end{align*}\]

105. Anthranilic acid, on treatment with iso-amyl nitrite furnishes a product which displays a strong peak at 76 (m/e) in its mass spectrum. The structure of the product is

\[\begin{align*}
\text{NO} & \quad \text{COOH} \\
\text{NO} & \quad \text{COOH} \\
\text{OH} & \quad \text{COOH} \\
\text{H}_2\text{N} & \quad \text{COOH} \\
\end{align*}\]
106. The organoborane $X$, when reacted with $\text{Et}_2\text{Zn}$ followed by $p$-iodotoluene in the presence of catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ furnishes a tri-substituted alkene. The intermediate and the product of the reaction, respectively, are

![Intermediate and product of the reaction](image)

107. Using Boltzmann distribution, the probability of an oscillator occupying the first three levels ($n = 0$, 1 and 2) is found to be $p_0 = 0.633$, $p_1 = 0.233$ and $p_2 = 0.086$.

The probability of finding an oscillator in energy levels in $n \geq 3$ is

- (a) 0.032
- (b) 0.048
- (c) 0.952
- (d) 1.000

108. The major products A and B in the following reaction sequence are

![Reaction sequence](image)
109. The correct combination of reagents required to effect the following conversion is

![Conversion Diagram]

(a) (i) Na, xylene, Me₃SiCl, heat; (ii) H₃O⁺
(b) (i) Na, xylene, heat; (ii) H₂O₂, NaOH
(c) (i) NaOEt, EtOH; (ii) Na, xylene, heat
(d) (i) TiCl₃, Zn–Cu, Me₃SiCl, heat; (ii) H₃O⁺

110. An organic compound gives following spectral data:
IR : 2210, 1724 cm⁻¹, ¹H NMR : δ 1.4 (t, J = 7.1 Hz, 3H), 4.4 (q, J = 7.1 Hz, 2H);
¹³C NMR : δ 16, 62, 118, 119, 125, 127, 168.
The compound is

(a) ![Structure A]
(b) ![Structure B]
(c) ![Structure C]
(d) ![Structure D]

111. The major product formed in the following reaction is

![Reaction Diagram]

(a) ![Product A]
(b) ![Product B]
(c) ![Product C]
(d) ![Product D]

112. The correct combination of reagents for effecting the following sequence of reactions is

![Reactions Diagram]

(a) A = O₂/O₃; B = K⁺·OOC-N=N-COO⁻·K⁺, AcOH
(b) A = O₂, Rose Bengal, hv; B = K⁺·OOC-N=N-COO⁻·K⁺, AcOH
(c) A = O₂, Rose Bengal, hv; B = H₂, Pd/C
(d) A = O₂, Rose Bengal; Δ ; B = H₂, Pd/C
113. The correct combination of reagents required to effect the following conversion is

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{O} \\
\text{I}
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{I}
\end{array}
\]

(a) \( \text{I}_2, \text{HNO}_3 \)  
(b) \( \text{s-BuLi, } -78^\circ\text{C followed by KI} \)  
(c) \( \text{NaOEt followed by ICH}_2\text{CH}_2\text{I} \)  
(d) \( \text{s-BuLi, } -78^\circ\text{C followed by ICH}_2\text{CH}_2\text{I} \)

114. Consider a particle confined in a cubic box. The degeneracy of the level, that has an energy twice that of the lowest level, is

(a) 3  
(b) 1  
(c) 2  
(d) 4

115. Only two products are obtained in the following reaction sequence. The structures of the products from the list I-IV are

(a) I and II  
(b) II and IV  
(c) I and III  
(d) III and IV

116. The major product A formed in the following reaction is

\[
\begin{array}{c}
\text{MeOC} \\
\text{COOMe}
\end{array}
\quad \text{Heat}
\begin{array}{c}
\text{COOMe}
\end{array}
\]

(a)  
(b)  
(c)  
(d)
117. The products A and B in the following reaction sequence are

\[
\text{SeO}_2 \xrightarrow{\text{dioxane reflux}} \text{(A) aq. NaCN, MnO}_2 \xrightarrow{\text{i-PrOH, Me}_2\text{NH}} \text{(B)}
\]

(a) A : \[
\begin{align*}
\text{CHO} \\
\end{align*}
\]

B : \[
\begin{align*}
\text{N} \\
\end{align*}
\]

(b) A : \[
\begin{align*}
\text{CHO} \\
\end{align*}
\]

B : \[
\begin{align*}
\text{O} \\
\end{align*}
\]

(c) A : \[
\begin{align*}
\text{CHO} \\
\end{align*}
\]

B : \[
\begin{align*}
\text{O} \\
\end{align*}
\]

(d) A : \[
\begin{align*}
\text{CHO} \\
\end{align*}
\]

118. The spatial part of the wave function of the atom in its ground state is 1s(1) 1s(2). The spin part would be

(a) \[\alpha(1)\alpha(2)\]

(b) \[\beta(1)\beta(2)\]

(c) \[\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]\]

(d) \[\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\]

119. The number of phases, components and degrees of freedom, when Ar is added to an equilibrium mixture of NO, O\(_2\) and NO\(_2\) in gas phase are, respectively,

(a) 1, 3, 5  
(b) 1, 4, 5  
(c) 1, 3, 4  
(d) 1, 4, 4

120. The major product formed in the following reaction is

(a) \[
\begin{align*}
\text{TsO} \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{OTs} \\
\end{align*}
\]

(c) \[
\begin{align*}
\text{OTs} \\
\end{align*}
\]

(d) \[
\begin{align*}
\text{OTs} \\
\end{align*}
\]

121. A particle in a one dimensional harmonic oscillator in x-direction is perturbed by a potential \(\lambda x \quad (\lambda \text{ is a number})\). The first-order correction to the energy of the ground state

(a) is zero  
(b) is negative  
(c) is positive  
(d) may be negative or positive but NOT zero.

122. The points A and B in the following sequence of reactions are

\[
\text{HO} \xrightarrow{\text{MeOH/H\textsuperscript{+} reflux, 24h}} \text{(A) PhCH(OMe)\textsubscript{2} (1 equiv)} \xrightarrow{\text{H\textsuperscript{+}}} \text{B}
\]

(a) \[
\begin{align*}
\text{HO} \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{OH} \\
\end{align*}
\]

(c) \[
\begin{align*}
\text{OH} \\
\end{align*}
\]

(d) \[
\begin{align*}
\text{OH} \\
\end{align*}
\]
123. The mass spectrum of the product A, formed in the following reaction, exhibits M, M+2, M + 4 peaks in the ratio of about 1 : 2 : 1. The reagent HX and the product A are

![Reaction Diagram]

(a) HX = HF and A = Br
(b) HX = HCl and A = Br
(c) HX = HBr and A = Br
(d) HX = HBr and A = Br

124. Match the following natural products in column A with their structural features in column B

**Column A**
(I) Colchicine
(II) Strychnine
(III) Quinine
(IV) Ephedrine

**Column B**
(A) Tetrahydrooxepine
(B) Phenanthrene
(C) Tropolone
(D) Phenylethylamine
(E) Quinoline
(F) Benzofuran

Identify the correct match from the following
(a) I-C, II-A, III-E, IV-D
(b) I-F, II-A, III-B, IV-E
(c) I-A, II-D, III-F, IV-D
(d) I-C, II-A, III-E, IV-F
125. A particle in a one-dimensional box (potential zero between 0 and infinite outside) has the ground state energy \( E_0 = \frac{0.125h^2}{ma^2} \). The expectation value of the above Hamiltonian with \( \psi(x) = x(x-a) \) yields an energy \( E_1 \). Using a linear combination of two even functions \( x(x-a) \) and \( x^2(x-a)^2 \), we obtain variational minimum to the ground state energy as \( E_2 \). Which of the following relations holds for \( E_0, E_1 \) and \( E_2 \)?
(a) \( E_0 < E_1 < E_2 \)  
(b) \( E_0 < E_2 < E_1 \)  
(c) \( E_1 < E_0 < E_2 \)  
(d) \( E_2 < E_0 < E_1 \)

126. The dissociation constant of a weak acid HX at a given temperature is \( 2.5 \times 10^{-5} \). The pH of 0.01 M NaX at this temperature is
(a) 7.3  
(b) 7.7  
(c) 8.3  
(d) 8.7

127. The ground state energy of hydrogen atom is \(-13.598 \text{ eV}\). The expectation values of kinetic energy, \( \langle T \rangle \) and potential energy, \( \langle V \rangle \), in units of eV, are
(a) \( \langle T \rangle = 13.598, \langle V \rangle = -27.196 \)  
(b) \( \langle T \rangle = -27.196, \langle V \rangle = 13.598 \)  
(c) \( \langle T \rangle = -6.799, \langle V \rangle = -6.799 \)  
(d) \( \langle T \rangle = 6.799, \langle V \rangle = -20.397 \)

128. If \( \psi = 0.8 \varphi_A + 0.4 \varphi_B \) is a normalized molecular orbital of a diatomic molecule AB, constructed from \( \varphi_A \) and \( \varphi_B \) which are also normalized, the overlap between \( \varphi_A \) and \( \varphi_B \) is
(a) 0.11  
(b) 0.31  
(c) 0.51  
(d) 0.71

129. At a given temperature consider
\[ \text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g}); K_1 = 0.05 \]
\[ 2\text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) + \text{O}_2(\text{g}); K_2 = 2 \times 10^{-12} \]
The equilibrium constant for the reaction
\[ 2\text{Fe}_2\text{O}_3(\text{s}) \rightarrow 4\text{Fe}(\text{s}) + 3\text{O}_2 \]
is
(a) \( 1 \times 10^{-13} \)  
(b) \( 2 \times 10^{-38} \)  
(c) \( 4 \times 10^{-15} \)  
(d) \( 2 \times 10^{-24} \)

130. In a bomb calorimeter, the combustion of 0.5 g of compound A (molar mass = 50 g mol\(^{-1}\)) increased the temperature by 4K. If the heat capacity of the calorimeter along with that of the material is 2.5 kJ K\(^{-1}\), the molar internal energy of combustion, in kJ, is
(a) 1000  
(b) -1000  
(c) 20  
(d) -20

131. The translational, rotational and vibrational partition functions for a molecule are
\( f_{\text{translation}} = 10^{10} \text{ m}^{-1}, f_{\text{rotation}} \approx f_{\text{vibration}} \approx 1, (k_B T / h) \approx 10^{13} \) at room temperature, \( N_A = 6 \times 10^{23} \)
Using the approximate data given above, the frequency factor (A) for a reaction of the type: atom + diatomic molecule \( \rightarrow \) non-linear transition state \( \rightarrow \) product, according to the conventional transition state theory is
(a) \( 2 \times 10^5 \)  
(b) \( 6 \times 10^7 \)  
(c) \( 2 \times 10^{12} \)  
(d) \( 6 \times 10^{13} \)
132. The interplanar spacing of (110) planes in a cubic unit cell with lattice parameter \( a = 4.242 \) Å is
(a) 5 Å (b) 6 Å (c) 7.35 Å (d) 2.45 Å

133. A compound \( A_x B_y \) has a cubic structure with \( A \) atoms occupying all corners of the cube as well as all the face centre positions. The \( B \) atoms occupy four tetrahedral voids. The values of \( x \) and \( y \) respectively, are
(a) 4, 4 (b) 4, 8 (c) 8, 4 (d) 4, 2

134. The number of lines in the ESR spectrum of \( CD_3 \) is (the spin of \( D \) is 1)
(a) 1 (b) 3 (c) 4 (d) 7

135. The number of lines in the ESR spectrum of \( CD_3 \) is (the spin of \( D \) is 1)
(a) 1 (b) 3 (c) 4 (d) 7

136. The fluorescence lifetime of a molecule in a solution is \( 5 \times 10^{-9} \) s. The sum of all of the non-radiative rate constants \( \sum k_{nr} \) for the decay of excited state is \( 1.2 \times 10^8 \) s\(^{-1} \). The fluorescence quantum yield of the molecule is
(a) 0.1 (b) 0.2 (c) 0.4 (d) 0.6

137. Solutions of three electrolytes have the same ionic strength and different dielectric constants as 4, 25 and 81. The corresponding relative magnitude of Debye-Hückel screening, lengths of the three solutions are
(a) 4, 25 and 81 (b) 2, 5 and 9 (c) 1/2, 1/5 and 1/9 (d) 1, 1 and 1

138. Simple Hückel molecular orbital theory
(a) considers electron-electron repulsion explicitly (b) distinguishes cis-butadiene and trans-butadiene (c) distinguishes cis-butadiene and cyclobutadiene (d) has different coulomb integrals for non-equivalent carbons.

139. For the non-dissociative Langmuir type adsorption of a gas on a solid surface at a particular temperature, the fraction of surface coverage is 0.6 at 30 bar. The Langmuir isotherm constant (in bar\(^{-1} \) units) at this temperature is
(a) 0.05 (b) 0.20 (c) 2.0 (d) 5.0

140. For a set of 10 observed data points, the mean is 8 and the variance is 0.04. The ‘standard deviation’ and the ‘coefficient of variation’ of the data are, respectively
(a) 0.005, 0.1% (b) 0.02, 0.2% (c) 0.20, 2.5% (d) 0.32, 1.0%

141. In the Lineweaver-Burk plot of (initial rate\(^{-1} \)) vs. (initial substrate concentration\(^{-1} \)) for an enzyme catalyzed reaction following Michaelis-Menten mechanism, the y-intercept is 5000 M\(^{-1} \) s. If the initial enzyme concentration is \( 9 \times 10^{-9} \) M, the turnover number is
(a) 2.5 \times 10^3 (b) 1.0 \times 10^4 (c) 2.5 \times 10^4 (d) 2.0 \times 10^5

142. The direct product in \( D_3 \) point group contains the irreducible representations
\[
\begin{array}{c|ccc}
& E & 2C_3 & 3C_2 \\
\hline
A_1 & 1 & 1 & -1 \\
A_2 & 1 & 1 & -1 \\
E_2 & 2 & -1 & 0 \\
\end{array}
\]
(a) \( A_1 + A_2 + E \) (b) \( 2A_1 + E \) (c) \( 2A_2 + E \) (d) \( 2A_1 + 2A_2 \)

143. The result of the product \( C_2(x)C_2(y) \) is
(a) \( E \) (b) \( \sigma_{xy} \) (c) \( C_2(z) \) (d) \( i \)
144. Given:
   A. \( \text{Fe(OH)}_2 (s) + 2e^- \rightarrow \text{Fe(s)} + 2\text{OH}^- (aq); \ E^0 = -0.877V \)
   B. \( \text{Al}^3+ (aq) + 3e^- \rightarrow \text{Al(s)}; \ E^0 = -1.66V \)
   C. \( \text{AgBr (aq)} + e^- \rightarrow \text{Ag(s)} + \text{Br}^- (aq); \ E^0 = 0.071V \)
   The overall reaction for the cells in the direction of spontaneous change would be
   (a) Cell with A and B: Fe reduced
       Cell with A and C: Fe reduced
   (b) Cell with A and B: Fe reduced
       Cell with A and C: Fe oxidized
   (c) Cell with A and B: Fe oxidized
       Cell with A and C: Fe oxidized
   (d) Cell with A and B: Fe oxidized
       Cell with A and C: Fe reduced

145. The reagent A used and the major product B formed in the following reaction sequence are

(a) A : LiAlH\(_4\)  
B : Br\(\text{CN} \)

(b) A : LiAlH\(_4\)  
B : NC\(\text{CN} \)

(c) A : NaBH\(_4\)  
B : Br\(\text{CN} \)

(d) A : H\(_2\)Pd – C

[Diagram of the reaction sequence]