Q. 1 – Q. 25 carry one mark each.

Q.1 [CpMoCl₂]₂ obeys the 18 electron rule. The correct structure of this compound is (atomic number of Mo = 42)



- Q.2 During oxygen transport by hemerythrin, oxygen is bound as
 - (A) O_2^- to one Fe(III) only (B) HO_2^- to one Fe(III) only (C) $O_2^{2^-}$ to one Fe(II) and one Fe(III) (D) $O_2^{2^-}$ to two Fe(II)
- Q.3 Among the following, the most stable isotope to radioactive decay is



- Q.4 At pH 7.2 and 10 Torr oxygen partial pressure, the extent of O₂ binding is
 - (A) high for both hemoglobin and myoglobin
 - (B) high for hemoglobin and low for myoglobin
 - (C) high for myoglobin and low for hemoglobin
 - (D) low for both hemoglobin and myoglobin
- Q.5 In the first row high-spin transition metal complexes $[M(H_2O)_6]Cl_2$ with d^5 and d^7 metal ions, the d-d transitions are
 - (A) spin-forbidden for both
 - (B) spin-allowed for both
 - (C) spin-forbidden for d^5 and spin-allowed for d^7
 - (D) spin-allowed for d^5 and spin-forbidden for d^7
- Q.6 Among the given boranes and heteroboranes, the example which belongs to 'closo' type is
 - (A) $B_5H_8^-$ (B) $[C_2B_9H_{11}]^{2-}$ (C) $GeC_2B_9H_{11}$ (D) B_6H_{10}



Q.7 The reaction of P_2O_5 with HNO₃ and HClO₄, respectively, gives

(A) NO₂ and ClO₂ (B) N₂O₅ and Cl₂O₆ (C) N₂O₃ and Cl₂O₇

(D) N_2O_5 and Cl_2O_7

- Q.8 When crystals of sodium chloride are heated in the presence of sodium vapor, they turn yellow. This is due to the formation of
 - (A) Schottky defects
 - (B) Frenkel defects
 - (C) F-centres
 - (D) H-centres
- Q.9 One mole of an ideal gas is compressed from 5 L to 2 L at constant temperature. The change in entropy, in J K⁻¹, of the gas is ______. (R = 8.314 J K⁻¹ mol⁻¹)
- Q.10 The linear momentum of a particle described by the wavefunction e^{-ikx} is

(A) <i>kh</i>	(B) - <i>kh</i>
(C) <i>kħ</i>	(D) $-k\hbar$

Q.11 For an elementary bimolecular gas phase reaction, activation energy is 5.5 kJ mol⁻¹. Enthalpy of activation, in kJ mol⁻¹, at 300 K is _____. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)







Q.13 Of the following inequalities, the criterion/criteria for spontaneity of a chemical reaction is/are (i) $(\Delta G)_{T,P} < 0$ (ii) $(\Delta U)_{S,V} > 0$ (iii) $(\Delta S)_{U,V} > 0$

(A)	(i) only	(B)	(ii) only	(C) (i) and (ii)	(D)	(i) and (i	iii)
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Q.14 A protein sample consists of an equimolar mixture of ribonuclease (molar mass = 13.7 kg mol⁻¹), hemoglobin (molar mass = 15.5 kg mol⁻¹), and myoglobin (molar mass = 17.2 kg mol⁻¹). The statement that is true about the weight-average molar mass ($\overline{M_w}$), the number-average molar mass ($\overline{M_n}$), and the polydispersity index (PDI) for this sample is

(A) $\overline{M_w} > \overline{M_n} = 15.5 \text{ kg mol}^{-1} \text{ and PDI} > 1$	(B) $\overline{M_w} > \overline{M_n} = 15.5 \text{ kg mol}^{-1} \text{ and PDI} < 1$
(C) $\overline{M_w} = 15.5 \text{ kg mol}^{-1} > \overline{M_n} \text{ and PDI} > 1$	(D) $\overline{M_w} = 15.5 \text{ kg mol}^{-1} < \overline{M_n} \text{ and PDI} < 1$



Q.15 The band structure given below represents a



(A) *n*-type semiconductor formed by doping Si with B (B) *n*-type semiconductor formed by doping Si with P

(C) *p*-type semiconductor formed by doping Si with P

(D) *p*-type semiconductor formed by doping Si with B

Q.16 The experimental ionization energies of hydrogen and helium atoms in their ground states are, respectively, 13.6 eV and 24.6 eV. The ground state energy of helium atom, in eV, is

$(A) - \frac{1}{2}(13.6) - 24.6$	(B) -4(13.6) - 24.6
$(C) - \frac{1}{4}(13.6) - 24.6$	(D) -2(13.6) - 24.6

Q.17 Ring flipping of the compound in the following conformation leads to



Q.18 The total number of lines expected (due to spin-spin coupling of proton with fluorine and deuterium nuclei) in the ¹H NMR spectrum of the following compound is ______.







Q.20 The most suitable reagent for performing the following transformation, is



Q.21 The major product obtained in the following reaction, is





Q.22 The favourable transition state leading to the formation of the product in the following reaction, is



Q.23 The major product of the following reaction, is





CH₃

Q.24 The major product obtained in the following reaction, is

$$H-C\equiv C-CH_{2}OH \qquad \begin{array}{c} 1. \text{ LiNH}_{2} (2 \text{ equiv.})/\text{liq. NH}_{3} \\ \hline 2.C_{2}H_{5}Br (1 \text{ equiv.}) \\ \hline 3. H_{3}O^{\oplus} \end{array}$$

$$(A) \qquad CH_{3}CH_{2}-C\equiv C-CH_{2}OH \qquad \begin{array}{c} (B) \\ H-C\equiv C-CH_{2}OCH_{2}CH_{3} \\ \hline (D) \\ H-C\equiv C-CH_{2}NH-CH_{2}CH_{3} \end{array}$$

Q.25 The major product formed in the following reaction, is





Q. 26 – Q. 55 carry two marks each.

- Q.26 The Larmor frequency of ¹H at 1 Tesla (T) is 42.57 MHz. If the magnetogyric ratios for ¹H and ¹³C are 26.75×10^7 rad T⁻¹ s⁻¹ and 6.72×10^7 rad T⁻¹ s⁻¹, respectively, the Larmor frequency of ¹³C, in MHz, at 1 Tesla will be ______.
- Q.27 At 1 bar and 298 K, for the process $A(s) \rightarrow A(l)$, the ΔG is 200 J mol⁻¹ and the ΔV_m is -2×10^{-6} m³ mol⁻¹. The minimum pressure, in bar, at which the process becomes spontaneous at 298 K is ______. (1 bar = 10⁵ Pa)
- Q.28 The reaction, $A \rightleftharpoons B$, is first order in both the directions. The forward and reverse rate constants are $4.2 \times 10^{-4} \text{ s}^{-1}$ and $1.04 \times 10^{-3} \text{ s}^{-1}$, respectively. The relaxation time for this reaction, in seconds, in a temperature jump experiment is ______.
- Q.29 Adsorption of CO on charcoal at 273 K follows Langmuir isotherm. A plot of P (kPa) / V (cm³) versus P (kPa) is linear with a slope of 0.01 and y-intercept of 0.5. The equilibrium constant, K (kPa⁻¹), for the adsorption is ______.
- Q.30 For the following reaction,

A + B
$$(k_1 = 10^5 \text{ L mol}^{-1} \text{ s}^{-1})$$
 I $(k_2 = 10 \text{ s}^{-1})$ P

if steady state approximation can be applied on [I], the observed rate constant of product formation, in L mol⁻¹ s⁻¹, will be ______.

Q.31 The correct set of infra-red spectral bands (in cm^{-1}) for the v_{CO} stretching mode of the given carbonyl complex is



(A) 1827, 1783, 1766
(B) 1973, 1827, 1794
(C) 1833, 1775, 1650
(D) 1960, 1918

- Q.32 The ¹⁹F NMR spectrum of ClF₃ when measured at -60 °C will be observed as a
 - (A) singlet
 - (B) doublet
 - (C) doublet and a triplet
 - (D) doublet of doublet and a doublet of triplet



Q.33 Among the given platinum(II) complexes, the one that is thermally the most unstable is



- Q.34 The shapes of XeF_5^+ and XeF_5^- , respectively, are
 - (A) pentagonal planar and square pyramidal
 - (B) pentagonal planar and trigonal bipyramidal
 - (C) square pyramidal and pentagonal bipyramidal
 - (D) square pyramidal and pentagonal planar
- Q.35 Sodium salts of pseudohalogens **X**, **Y**, and **Z** form colourless solutions in water. Solution of **X** decolorizes I_3^- solution with brisk effervescence. Solution of **Y** gives an intense red colour on reaction with Fe^{3+} solution. Solution of **Z** gives an intense blue colour on reaction with a solution containing Fe^{3+} and Fe^{2+} ions. The pseudohalogens **X**, **Y**, and **Z**, respectively, are

(A) CN⁻, N₃⁻, and CNS⁻
(B) N₃⁻, CNS⁻, and CN⁻
(C) N₃⁻, CN⁻, and CNS⁻
(D) N₃⁻, CNS⁻, and CNO⁻

Q.36 On reacting 1.55 g of a diol with an excess of methylmagnesium iodide, 1.12 L (corrected to STP) of methane gas is liberated. The molecular mass (g mol⁻¹) of the diol is ______.



Q.37 The structure of the compound having the following characteristic spectral data, is IR: 1690 cm⁻¹;

¹H-NMR: 1.30 (3H, t, *J* = 7.2 Hz); 2.41 (2H, q, *J* = 7.2 Hz); 2.32 (3H, s); 7.44 (1H, t, *J* = 7.0 Hz); 7.57 (1H, dt, *J* = 7.0, 3.0 Hz); 7.77 (1H, t, *J* = 3.0 Hz); 7.90 (1H, dt, *J* = 7.0, 3.0 Hz); EI Mass: m/z 119 (100%); 57 (80%).





Q.38 The major products **X** and **Y** formed in the following synthetic scheme, are





Q.39 The major products **S** and **T** formed in the following synthetic scheme, are





Among the following, the transformation(s) that can be accomplished using *umpolung* concept Q.40 is(are)



Q.41 A disaccharide does NOT give a positive test for Tollen's reagent. Upon acidic hydrolysis, it gives an equimolar mixture of two different monosaccharides, both of which can be oxidized by bromine water. This disaccharide is



(C) (ii) only



(B)



(C)



(D)





Q.42 The major products **M** and **N** in the following reaction sequence are







Q.43 The major products **P** and **Q** in the following reaction sequence, are

Q.44 The major product formed in the following reaction, is





Q.45 The following synthetic transformation can be achieved using



Reagents: (p) (i) NH_2OH/H^+ , (ii) H_2SO_4 (q) HN_3/H^+ (r) (i) NH_2OH/H^+ , (ii) NaOH

- (A) (p) only
- (B) (p) and (q)
- (C) (q) and (r)
- (D) (r) only
- Q.46 Consider a two-state system at thermal equilibrium with equal degeneracy where the excited state is higher in energy than the ground state by 0.1 eV. The ratio of the population of the excited state to that of the ground state, at a temperature for which $k_BT = 0.05$ eV, is _____.
- Q.47 Of the vibrational modes given below, the IR active mode(s) is(are)



Q.48 A system is described by the following real wavefunction.



The probability (P) of finding the particle in a region dx around points I, II, and III in the figure obeys the trend

(A) $P(I) > P(II) > P(III)$	(B) $P(II) > P(III) > P(I)$
(C) $P(II) > P(I) > P(III)$	(D) $P(\text{III}) > P(\text{I}) > P(\text{II})$



Q.49 The temperature-composition (T-x) phase diagram of the two-component system made of X and Y is given below. At a temperature of 288 K and starting at the point P, Y is added until the composition reaches S. Which of the following statements is NOT TRUE?



- (A) At P, the solid and liquid are present in almost equal proportions.
- (B) At Q, the system is all liquid.
- (C) At S, the system has more solid than liquid.
- (D) At R, the liquid is pure X.
- Q.50 For a system subjected to only P-V work, entropy is given by

(i) $-\left(\frac{\partial G}{\partial T}\right)_P$ (ii) $\left(\frac{\partial G}{\partial P}\right)_T$ (iii) $-\left(\frac{\partial A}{\partial V}\right)_T$ (iv) $-\left(\frac{\partial A}{\partial T}\right)_V$ (A) (i) and (ii) (B) (i) and (iv) (C) (i) only (D) (ii) only

- Q.51 According to Irving-Williams series, the number of *d* electrons for the first row transition metal (M) ion having the highest overall stability constant $(\log \beta)$ for $[M(EDTA)]^{2-}$ is _____.
- Q.52 The magnitude of the difference in the crystal field stabilization energies, in Δ_o (ignoring pairing energy), of $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ is _____.
- Q.53 The calculated and observed magnetic moments differ considerably for an aqua complex of a lanthanide(III) ion as a result of low lying states of high *J*. The ion, among the following, is

(A)
$$Ce^{3+}$$
 (B) Pr^{3+} (C) Eu^{3+} (D) Yb^{3}

Q. 54. In the electronic spectrum of $[CrF_6]^{3-}$, absorption bands observed at 670, 440, and 290 nm are, respectively, due to the transitions

 $\begin{array}{lll} (A) \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(P), & \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(F) & and \ \ ^{4}A_{2g} \rightarrow \ ^{4}T_{2g} \\ (B) \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(P), & \ ^{4}A_{2g} \rightarrow \ ^{4}T_{2g} & and \ \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(F) \\ (C) \ \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(F), & \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(P) & and \ \ ^{4}A_{2g} \rightarrow \ ^{4}T_{2g} \\ (D) \ \ ^{4}A_{2g} \rightarrow \ ^{4}T_{2g}, & \ \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(F) & and \ \ \ ^{4}A_{2g} \rightarrow \ ^{4}T_{1g}(P) \end{array}$



Q. 55. Amongst the following, the group that is bound to the metal ion in coenzyme B_{12} is

- (A) methyl(B) cyanide(C) adenosyl
- (D) hydroxyl

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END OF THE QUESTION PAPER

