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<u>Q.1 – Q.15 Multiple Choice Question (MCQ), carry ONE mark each</u> (for each wrong answer: – 1/3).

1. The major product-M formed in the following reaction is



2. The starting material-Y in the following reaction is



- 3. The major product in the given reaction is Q. The mass spectrum of Q shows
 - [M] = molecular ion peak

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- (a) [M], [M+2] and [M+4] with relative intensity of 1:2:1
- (b) [M] and [M+2] with relative intensity of 1:1
- (c) [M], [M+2] and [M+4] with relative intensity of 1:3:1
- (d) [M] and [M+2] with relative intensity of 2:1
- 4. A tripeptide on treatment with PhNCS (pH = 8.0) followed by heating with dilute HCl afforded a cyclic compound-M and a dipeptide. The dipeptide on treatment with PhNCS (pH = 8.0) followed by heating with dilute HCl afforded a cyclic compound-N and an acyclic compound-O. The CORRECT sequence (from N- to Cterminus) of the tripeptide is,





5. The major product-M in the following reaction is



6. The major product-T formed in the following reaction is



7. In differential thermal analysis (DTA) 27-0019

- (a) the temperature differences between the sample and reference are measured as a function of temperature
- (b) the differences in heat flow into the reference and sample are measured as a function of temperature
- (c) the change in the mass of the sample is measured as a function of temperature
- (d) the glass transition is observed as a sharp peak
- 8. The v₀₋₀ resonance Raman stretching frequency (cm⁻¹) of the coordinated dioxygen in oxy-hemoglobin and oxy-hemocyanin appears, respectively, nearly at (a) 1136 and 744 (b) 1550 and 744 (c) 744 and 1136 (d) 744 and 1550
- 9. The number of metal-metal bond(s), with σ, π and δ character, present in [Mo₂(CH₃CO₂)₄] complex is(are), respectively,
 (a) 1, 2, 1
 (b) 1, 2, 0
 (c) 1, 1, 0
 (d) 1, 1, 1
- 10. $1s_A$ and $1s_B$ are the normalized eigen functions of two hydrogen atoms H_A and H_B , respectively. If $S = \langle 1s_A | 1s_B \rangle$, the option that is ALWAYS CORRECT is

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(a) $C = 1$	$(\mathbf{b}) \mathbf{c} = 0$	(a) C - imaginamy constant	(d) 0 - 0 - 1
(a) 5 - 1	(0) 3 = 0	(C) S – Illiagillary collstant	$(\mathbf{u}) 0 \leq 3 \leq 1$

11. The pure vibrational spectrum of a hypothetical diatomic molecule shows three peaks with the following intensity at three different temperatures.

Peak	Intensity (arbitrary unit)									
	300 K	600 K	900 K							
Ι	1.0	1.0	1.0							
II	0.1	0.1	0.1							
III	0.02	0.04	0.06							

The CORRECT statement is

(a) Peak I appears at the lowest energy (b) Peak II appears at the lowest energy

(c) Peak III appears at the lowest energy (d) Peak I appears at the highest energy

- **12.** The point group of SF_6 is
- (a) D_{6h}
 (b) Oh
 (c) D_{6d}
 (d) C_{6v}
 13. A point originally at (1, 3, 5) was subjected to a symmetry operation (O
 1) that shifted the point to (-1, -3, 5). Subsequently, the point at (-1, -3, 5) was subjected to another symmetry operation (O
 2) that shifted this point to (-1, -3, -5). The symmetry operators O
 1 and O
 2 are, respectively,

(a) $\widehat{C_2}(x)$ and $\widehat{\sigma}(xy)$ (b) $\widehat{C_2}(z)$ and $\widehat{\sigma}(xy)$ (c) $\widehat{\sigma}(xy)$ and $\widehat{C_2}(z)$ (d) $\widehat{S_1}$ and $\widehat{S_2}$

- 14. Adsorption of a gas with pressure-P on a solid obeys the Langmuir adsorption isotherm. For a fixed fractional coverage, the correct relation between K and P at a fixed temperature is [K = ka/kb, where ka and kb are the rate constants for adsorption and desorption, respectively. Assume non-dissociative adsorption.]

 (a) k ∝ p^{-1/2}
 (b) k ∝ p
 (c) k ∝ p⁻¹
 (d) k ∝ p^{1/2}
- 15. The temperature dependence of the rate constant for a Second-order chemical reaction obeys the Arrhenius equation. The SI unit of the 'pre-exponential factor' is

 (a) s⁻¹
 (b) m³mol⁻¹s⁻¹
 (c) mol m⁻³s⁻¹
 (d) (m³mol⁻¹)²s⁻¹

 Q.16 Q.22 Multiple Select Question (MSQ), carry ONE mark each (no negative marks).
- **16.** The CORRECT reagent(s) for the given reaction is(are)



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(b)

- (a) H_2O_2 , NaOH
- (c) DIBAL-H, then mCPBA

(d) SO_3 , pyridine, Me_2SO

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17. The CORRECT statement(s) about the ¹H-NMR spectra of compounds P and Q is (are)



- (a) P shows a sharp singlet at $\delta=3.70$ ppm (for H_a and $H_b)$
- (b) Q shows a sharp singlet at $\delta = 3.70$ ppm (for H_a and H_b)
- (c) P shows a AB-quartet centered at $\delta = 3.63$ ppm (for H_a and H_b)
- (d) Q shows a AB-quartet centered at $\delta = 3.63$ ppm (for H_a and H_b)
- 18. The CORRECT statement(s) about thallium halides is(are)
 - (a) TIF is highly soluble in water whereas other Tl-halides are sparingly soluble
 - (b) TIF adopts a distorted NaCl structure
 - (c) TlL₃ is isomorphic with CsL₃ and the oxidation state of Tl is +3
 - (d) Both TlBr and TlCl have CsCl structure
- 19. The CORRECT statement(s) about the spectral line broadening in atomic spectra is(are)
 - (a) The collision between atoms causes broadening of the spectral line
 - (b) Shorter the lifetime of the excited state, the broader is the line width
 - (c) Doppler broadening is more pronounced as the flame temperature increases
 - (d) In flame and plasma, the natural line broadening exceeds the collisional line broadening
- 20. Match the CORRECT option(s) from column-A with column-B according to the metal centre present in the active site of metalloenzyme.

	Column-A		Column-B
Р.	Cu	I.	B ₁₂ -coenzyme
Q.	Мо	II.	Carboxypeptidase
R.	Со	III.	Nitrate reductase
S.	Zn	IV.	Cytochrome P-450
		V.	Tyrosinase

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	Р		Q		R		S
a)	V	;	III	;	Ι	;	II
	II	;	IV	;	V	;	III

21. The CORRECT statement(s) about the following phase diagram for a hypothetical pure substance "X" is(are)



- (a) The molar volume of solid-X is less than the molar volume of liquid X
- (b) X does not have a normal boiling point
- (c) The melting point of X decreases with increase in pressure
- (d) On increasing the pressure of the gas isothermally, it is impossible to reach solid phase before reaching liquid phase
- 22. The parameter(s) fixed for each system in a canonical ensemble is(are)
 - (a) temperature (b) pressure (c) volume (d) composition

<u>Q.23 – Q.25 Numerical Answer Type (NAT), carry ONE mark each (no</u> <u>negative marks).</u>

23. The number of peaks exhibited by T in its broadband proton decoupled ¹³C-NMR spectrum recorded at 25 °C in CDCl₃ is _____



24. The diffraction angle of (321) sets of plane of a metal with atomic radius 0.125 nm, and adopting BCC structure is ________ degree (rounded off to one decimal place)

(Given: the order of reflection is 1 and the wavelength of X-ray is 0.0771 nm)

25. For the angular momentum operator L and the spherical harmonics

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 $Y_{lm}(\theta, \phi), (\hat{L}_x^2 + \hat{L}_y^2) Y_{21}(\theta, \phi) = n\hbar^2 Y_{21}(\theta, \phi).$ The value of *n* is

Q.26 - Q.40 Multiple Choice Question (MCQ), carry TWO mark each

(for each wrong answer: - 2/3).

26. The major product-P obtained in the following reaction sequence is



28. The major product-P in the following reaction is



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29. The major product-P in the reaction sequence is



30. The major products P and Q in the following reaction sequence are



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31. The major products M and N in the given reaction sequence are



32. Three different crystallographic planes of a unit cell of a metal are given below (solid circles represent atom). The crystal system of the unit cell is



(a) triclinic
(b) monoclinic
(c) tetragonal
(d) orthorhombic

33. The number of equivalents of H₂S gas released from the active site of rubredoxin,
2-iron ferredoxin and 4-iron ferredoxin when treated with mineral acid,
respectively, are

(a) 4, 6, 8 (b) 0, 2, 4 (c) 1, 2, 4 (d) 0, 2, 3

34. The number of v_{S=0} stretching vibration band(s) observed in the IR spectrum of the high-spin [Mn(dmso)₆]³⁺ complex is (dmso: dimethylsulfoxide)
(a) only one (b) two with intensity ratio 1:2

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(c) two with intensity ratio 1:1

(d) six with intensity ratio 1:1:1:1:1

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35.
$$[Fe(H_2O)_6]^{2+} + [Fe^*(H_2O)_6]^{3+} \xrightarrow{k_{11}} [Fe(H_2O)_6]^{3+} + [Fe^*(H_2O)_6]^{2+}$$

 $[Fe(bpy)_3]^{2+} + [Fe^*(bpy)_3]^{3+} \xrightarrow{k_{22}} [Fe(bby)_3]^{3+} + [Fe^*(bby)_3]^{2+}$
 $[Co(NH_3)_6]^{2+} + [Co^*(NH_3)_6]^{3+} \xrightarrow{k_{33}} [Co(NH_3)_6]^{3+} + [Co^*(NH_3)_6]^{2+}$
*indicates a radioactive isotope & (bby = bipyridyl)

The rate constants in the given self-exchange electron transfer reactions at a certain temperature follow

- (a) $k_{11} > k_{22} > k_{33}$ (b) $k_{22} > k_{11} > k_{33}$ (c) $k_{33} > k_{22} > k_{11}$ (d) $k_{22} > k_{33} > k_{11}$
- 36. The CORRECT distribution of the products in the following reaction is



37. The addition of $K_4[Fe(CN)_6]$ to a neutral aqueous solution of the cationic species of a metal produces a brown precipitate that is insoluble in dilute acid. The cationic species is

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(a)
$$Fe^{3+}$$
 (b) UO_2^{2+} (c) Th^{4+} (d) Cu^{2+}

38. The electronic spectrum of a Ni(II) octahedral complex shows four d-d bands, labelled as P, Q, R and S. Match the bands corresponding to the transitions.

				λ _{ma}	_{ax} , ni	m (ε, M ⁻¹	cm ⁻¹))		Tr	ans	sitio	ons					
]	P.	100	0 (5	0)				I.	³ A	2g(F)	\rightarrow ³ T	1g(l	P)			
		(Q.	770	(8)					II.	³ A	2g(F) ·	→ ³ 1	1g(l	F)			
]	R.	630	(55))				III.	³ A	2g(F) ·	→ ³ 1	2 _{2g} (1	F)			
		5	5.	375	(11	0)				IV.	³ A	2g(F) ·	$\rightarrow {}^{1}\mathbf{E}$	c _g (D)			
										l									
	P	•	Q		R		S	rF &	7.4		F	•		Q		R		S	
	(a) IV	/ ;	III	;	II	; (b BA	169	JAA	(b)	Π	Ι	;	IV	;	II	;	Ι	
	(c) I	[;	IV	;	K	;	ш			(d)	Ì		;	IV	;	II	;	III	
39.	In the f	ollowi	ng	table	, the	e le	ft colu	mn rej	prese	ents t	he	rigi	d-r	otor	typ	e ar	nd t	he ri	ight
	column shows a set of molecules.																		
		Р.	Sy	ymm	etric	e ro	tor (ol	olate)	2		.5	Si	H4						
		Q.	Sy	ymm	etric	e ro	tor (pi	rolate)	\square		I.	CI	H ₃ C	21					
		R.	SI	pheri	ical 1	rote	or	\sim		I	Π.	C ₆	H ₆						
		S.	A	symr	netr	ic r	otor			193 <mark>1</mark>	V.	CI	1 ₃ 0)H					
				1	-			×ing	, o		V .	CC	D ₂						
	The CO	RRE	CT	mate	ch is			. 212			E	\mathcal{V}	*						
	P	•	Q		R	2	S	1 A	C	AL	1	P		Q		R		S	
	(a) I	;	II	;	III	;	IV			(b)	Ι	II	;	II	;	Ι	;	IV	_
	(c) II	Ι;	V	;	Ι	;	II			(d)	V	V	;	IV	;	III	;	II	
40.	The CO	RRE	CT	state	men	t re	egardi	ng the	follo	wing	thr	ee 1	nor	mal	mo	des o	of v	ibra	tion

of SO_3 is



(a) (I) and (II) are infrared active while (III) is infrared inactive

(b) (I) is infrared inactive while (II) and (III) are infrared active



(c) (I) and (III) are infrared inactive while (II) is infrared active

(d) None of the modes are infrared active since SO_3 has zero dipole moment

<u>Q.41 – Q.46 Multiple Select Question (MSQ), carry TWO mark each</u> (no negative marks).

41. The reaction(s) that yield(s) **3-phenylcyclopentanone** as the major product is(are)



42. The reaction(s) that yield(s) M as the major product is(are)



43. The CORRECT statement(s) regarding $B_{10}H_{14}$ is(are)

(b) 10 N H₂SO₄, -10 °C

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- (a) Brønsted acidity of $B_{10}H_{14}$ is higher than that of B_5H_9
- (b) Structurally $B_{10}H_{14}$ is a closo-borane
- (c) The metal-promoted fusion of $B_5 H_8^-$ produces $B_{10} H_{14}$
- (d) Both $B_{10}H_{14}$ and $B_{10}H_{12}(SEt_2)_2$ have the same number of valence electrons

44. The CORRECT statement(s) about the Group-I metals is(are)

- (a) Reactivity of Group-I metals with water decreases down the group
- (b) Among the Group-I metals, Li spontaneously reacts with N_2 to give a red-brown layer-structured material
- (c) Thermal stability of Group-I metal peroxides increases down the group
- (d) All the Group-I metal halide are high-melting colorless crystalline solids
- 45. The compound(s) that satisfies/satisfy the 18-electron rule is(are)



48. The calculated magnetic moment of a Ce³⁺ complex is _____

_BM (rounded off

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to two decimal places)

49. The state of the electron in a He⁺ ion is described by the following normalized wavefunction,

$$\varphi(r,\theta,\varphi) = \sqrt{\frac{3}{8}}R_{21}(r)Y_{10}(\theta,\varphi) - i\sqrt{\frac{7}{16}}R_{10}(r)Y_{00}(\theta,\varphi) + xR_{32}(r)Y_{20}(\theta,\varphi)$$

Here, R_{nl} and Y_{lm} represent the radial and angular components of the eigenfunctions of He⁺ ion, respectively, and *x* is an unknown constant. If the energy of the ion is measured in the above state, the probability of obtaining the energy of $-\frac{2}{9}$ atomic unit is ______(rounded off to two decimal places)

50. A certain wavefunction for the hydrogen-like atom is given by

$$\varphi(\mathbf{r},\theta,\phi) = \frac{2^{\frac{1}{2}}}{81\pi^{\frac{1}{2}}} \left(\frac{\mathbf{Z}}{\mathbf{a}_{0}}\right)^{5/2} \left(6 - \frac{\mathbf{Zr}}{\mathbf{a}_{0}}\right)\mathbf{r} - e^{-\mathbf{Zr}/3\mathbf{a}_{0}}\cos\theta$$

The number of node(s) in this wavefunction is

- 51. EMF of the following cell: Cu | CuSo_{4(aq,1.0 mol/kg)} | Hg₂SO_{4(s)} | Hg_(l) |Pt at 25 °C and 1 bar is 0.36 V. The value of the mean activity coefficient of CuSO₄ at 25 °C and 1 bar is ______(rounded off to three decimal places) [Given: Standard electrode potential values at 25 °C for Cu²⁺ + 2e⁻ \rightarrow Cu and Hg₂SO₄ + 2e⁻ \rightarrow 2Hg + SO₄²⁻ are 0.34 V and 0.62 V, respectively. Consider: RT/F at 25 °C = 0.0256 V]
- 52. The radius of gyration for three-dimensional random coil linear polyethylene of molecular weight 8,40,000 is _____nm (rounded off to one decimal place)

[Given: C−C bond length = 0.154 nm]
53. The activation energy of the elementary gas-phase reaction O₃ + NO → NO₂ + O₂ is 10.5 kJ mol⁻¹. The value of the standard enthalpy of activation at 25 °C is _____ kJ mol⁻¹ (rounded off to two decimal places, Given: R = 8.314 J mol⁻¹K⁻¹]

- 54. In a collection of molecules, each molecule has two non-degenerate energy levels that are separated by 5000 cm^{-1} . On measuring the population at a particular temperature, it was found that the ground state population is 10 times that of the upper state. The temperature of measurement is _____K (rounded off to the nearest integer, Given: Value of the Boltzmann constant = 0.695 cm^{-1}K^{-1}]
- 55. The change in entropy of the surroundings to convert 1 mol of supercooled water at



263 K to ice at 263 K at 1 bar is _____J K⁻¹ (rounded off to two decimal places) [Consider: $\Delta_{fus}H^0$ at 273 K = 6.0 kJ mol⁻¹, and the molar heat capacity of water is higher than that of ice by 37.0 J K⁻¹ mol⁻¹ in the temperature range of 263 K to 273 K]

Q.No	Ans		Q.No	Ans		Q.No	Ans
1.	b		21.	b & c		41.	a & b
2.	b		22.	a & c & d		42.	a & b & d
3.	a		23.	8		43.	a & c & d (OR) a & c
4.	a		24.	$59 ext{ to } 61$		44.	b & c & d
5.	a	N.	25.	5	. 6.	45.	a & d
6.	a	R	26.	a	S	46.	b & d
7.	a	ر S	27.	a	R	47.	1
8.	a		28.	a		48.	2.52 to 2.56
9.	a		29.	a		49.	0.18 to 0.20
10.	d		30.	b		50.	2
11.	С		31.	b		51.	0.042 to 0.046
12.	b		32.	d		52.	15.2 to 15.6
13.	b	10	33.	b	2	53.	5.50 to 5.60
14.	С	У Г	34.	b		54.	3100 to 3150
15.	b		35.	b		55.	21.20 to 21.60
16.	a & b		36.	С			
17.	a & d		37.	d			
18.	a & b & d		38.	b			
19.	a & b & c		39.	b			
20.	a		40.	b			

Answer Key

Q. 1 – 15	1 Mark	Q. 16 – 22	1 Mark	Q. 23 – 25	1 Mark
	(MCQ)		(MSQ)		(NAT)
Q. 26 – 40	2 Mark	Q. 41 – 46	2 Mark	Q. 47 – 55	2 Mark
	(MCQ)		(MSQ)		(NAT)

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