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Attempt ALL the questions. Q.1 – Q.10 Multiple Choice Question (MCQ), carry ONE mark each (for each wrong answer: - 1/3). The **CORRECT** order of **pK**_a for the compounds I to IV in water at 298 K is 1. $HCo(CO)_4$ $HCo(CO)_3(PPh_3)$ $HCo(CO)_3(P(OPh)_3)$ $HCo(CO)_2(PPh_3)_2$ Ι Π IV III (a) I > II > III > IV (b) IV > III > II > I(d) I > III > II > IV (c) IV > II > III > IFor Na⁺, Mg²⁺, Al³⁺ and F⁻ the CORRECT order of ionic radii is 2. (a) $Al^{3+} > Mg^{2+} > Na^{+} > F^{-}$ (b) $Al^{3+} > Na^{+} > Mg^{2+} > F^{-}$ (c) $F^- > Na^+ > Mg^{2+} > Al^{3+}$ (d) $Na^+ > F^- > Mg^{2+} > Al^{3+}$ Spin-only magnetic moments (in BM) of $[NiCl_2(PPh_3)_2]$ and $[Mn(NCS)_6]^{4-}$, 3. respectively, are (b) 2.83 and 1.89 (c) 0.00 and 1.89 (a) 0.00 and 5.92 (d) 2.83 and 5.92 4. Two sets of quantum numbers with the same number of radial nodes are (a) n = 3; l = 0; $m_l = 0$ and n = 2; l = 0; $m_l = 0$ (b) n = 3 ; l = 1 ; $m_l = 1$ and n = 2 ; l = 1 ; $m_l = 0$ (c) n = 3 ; l = 2 ; $m_l = 0$ and n = 2 ; l = 1 ; $m_l = 0$ (d) n = 3; l = 1; $m_l = -1$ and n = 2; l = 1; $m_l = 0$ 5. The major product formed in the following reaction is CF₃COOH / H₂O CHCl₃, 0 °C, 1 h CH_3C (b) (a) (d) (c) Tiruchirappalli - 620 024 www.csircoaching.com ajchemacademy@gmail.com

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6. The Major product formed in the following reaction is



7. The structure that corresponds to the following ¹H-NMR spectral data is ¹H NMR : δ 7.31 (2H), 7.21 (2H), 4.5 (2H) and 2.3 (3H)



9. A pure substance M has lesser density in solid state than in liquid state. The ΔS_{fusion} of M is +25 JK⁻¹ mol⁻¹. The CORRECT representative Pressure-Temperature diagram for the fusion of M is



0

8.



10. Among the following, the matrices with non-zero determinant are

	Р	Q	R	S								
	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 4 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 \\ 3 & 1 & 3 & 0 \\ 4 & 3 & 1 & 4 \end{bmatrix}$	$\begin{bmatrix} 1 & 2 & 3 & 1 \\ 2 & 3 & 4 & 2 \\ 3 & 4 & 1 & 3 \\ 4 & 1 & 2 & 4 \end{bmatrix}$								
	(a) P, Q and R	(b) P, R and S	(c) P, Q an	nd S (d) Q, R and S								
	Attempt ALL the	<u>e questions. Q</u>	.11 – Q.30 Mul	tiple Choice Question								
	(MCQ), carry TWO mark each (for each wrong answer: – 2/3).											
11.	Reaction of BCl ₃ with NH ₄ Cl at 140 °C produces compound P. Further, P reacts											
	with $NaBH_4$ to give a colorless liquid Q. The reaction of Q with H_2O at 100 °C											
	produces compound R and a diatomic gas S. Among the following, the CORRECT											
	statement is											
	(a) P is $B_3N_3H_6$	(b) R is [B(OH)N	$[H]_3 \qquad (c) Q is$	$[BCINH]_3 \qquad (d) S is Cl_2$								
12.	The complex that do	es NOT obey the	18-electron rule is									
	(Given: Atomic num	bers of Ti, Mn, Ta	a and Ir are 22, 25	5,73 and 77, respectively)								
	(a) $[(\eta^5 - C_5 H_5) Ti(CO)]$)4]-	(b) [Mn(SnPh ₂	$_{3})_{2}(CO)_{4}]^{-}$								
	(c) $[(\eta^5 - C_5 H_5) Ir(CH_2)]$	2)(PMe ₃)]	(d) [TaCl ₃ (PEt	$(CHCMe_3)_2(CHCMe_3)]$								
13.	Hybridization of the	central atoms in	I_3^- , ClF ₃ and SF ₄ , r	espectively, are								
	(a) sp^3d , sp^2 and dsp	2	(b) sp, sp ³ d	and dsp ²								
	(c) sp^3d , sp^3d and sp	³ d	(d) sp, sp ² a	and sp ³ d								
14.	Reaction of [Ni(CN	$]_4]^{2-}$ with metall	ic potassium in l	iquid ammonia at −33 °C								
	yields complex E. The geometry and magnetic behavior of E, respectively, are											
	(a) Square planar and	diamagnetic	(b) Tetrahedral a	nd diamagnetic								
	(c) Octahedral and paramagnetic (d) Square pyramidal and paramagnetic											
15.	The decreasing orde	r of C=C bond le	ngth in the followi	ng complexes is								
	$[Cl_3Pt(H_2O)]$	$C=CH_2)]^-$	$[Cl_3Pt((CN)_2C=C(CN)_2)]^-$									
	1	[Π								

0

$[Cl_3Pt(F_2C=CH_2)]^-$	
III	

$$[Cl_3Pt(F_2C=CF_2)]^-$$
IV

4

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

16. The CORRECT combination for metalloenzymes given in Column I with their catalytic reactions in Column II is

	Column I		Column II							
(K)	Cytochrome P-450	(i)	$2H_2O_2 \rightarrow 2H_2O + O_2$							
(L)	Catalase	(ii)	$\mathbf{R} - \mathbf{C}\mathbf{H}_{2}\mathbf{O}\mathbf{H} + \mathbf{O}_{2} \longrightarrow \mathbf{R} - \mathbf{C}\mathbf{H}\mathbf{O} + \mathbf{H}_{2}\mathbf{O}_{2}$							
	24	3ATE ($(\mathbf{R} = \mathbf{alkyl} \text{ or aryl})$							
(M)	Galactose oxidase	(iii)	$0_2 + 4H^+ + 4e^- \rightarrow 2H_2O$							
(N)	Cytochrome c oxidase	(iv)	$\mathbf{R} - \mathbf{H} + \mathbf{O}_2 + 2\mathbf{e}^- + 2\mathbf{H}^+ \longrightarrow \mathbf{R} - \mathbf{OH} + \mathbf{H}_2\mathbf{O}$							
	IS IN	X	$(\mathbf{R} = \mathbf{alkyl} \text{ or aryl})$							
	K L M	N	K L M N							
(a)	(iii) ; (iv) ; (i) ; ((ii)	(b) (iv) ; (ii) ; (i) ; (iii)							
(c)	(iv) ; (i) ; (ii) ; (ii)	(iii)	(d) (iii) ; (i) ; (ii) ; (iv)							

17. According to the crystal field theory, d-d transition observed in [Ti(H₂O)₆]³⁺ is
(a) Laporte forbidden and spin forbidden
(b) Laporte allowed and spin forbidden
(c) Laporte allowed and spin allowed
(d) Laporte forbidden and spin allowed

18. The major product formed in the following reaction sequence is



0



19. The products P, Q, R and S formed in the following reactions are



(a)
$$E = Br \bigvee_{H}^{N} Br$$
 and $F = \bigvee_{N}^{Br}$
(b) $E = \bigvee_{H}^{N} Br$ and $F = \bigvee_{N}^{Br} Br$

(c)
$$E = \bigvee_{\substack{N \\ H}}^{Br} Br$$
 and $F = \bigvee_{\substack{N \\ N}}^{Br}$

5



20.

21. The reaction that produces the following as a major product is



22. The major product formed in the following reaction is



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23. The major product formed in the following reaction is

25. Monochromatic X-rays having energy 2.8 × 10⁻¹⁵ J diffracted (first order) from (200) plane of a cubic crystal at an angle 8.5°. The length of unit cell in Å of the crystal is_____ (rounded off to one decimal place)

(Given: Planck's constant,
$$h = 6.626 \times 10^{-34}$$
 J s; $c = 3.0 \times 10^8$ m s⁻¹)
(a) 2.4 (b) 3.4 (c) 4.8 (d) 9.8

26. For $\alpha > 0$, the value of the integral $\int_{-\infty}^{+\infty} x e^{-\alpha x^2} dx$ is

(a)
$$\sqrt{\frac{\pi}{\alpha}}$$
 (b) ∞ (c) 0 (d) 1

27. The volume correction factor for a non-ideal gas in terms of critical pressure (p_c), critical molar volume (V_c) critical temperature (T_c) and gas constant (**R**) is



(a) $\frac{\mathrm{RT}_{\mathrm{c}}}{\mathrm{8p}_{\mathrm{c}}}$	(b) $\frac{27 \text{ R}^2 \text{T}_c^2}{64 \text{p}_c}$	$(c) \frac{8p_cV_c}{3T_c}$	(d) $3p_c V_c^2$
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28. Half-life $(t_{1/2})$ of a chemical reaction varies with the initial concentration of reactant (A_0) as given below:

$A_0 \ (mol \ L^{-1})$	$5 imes 10^{-2}$	$4 imes 10^{-2}$	$3 imes 10^{-2}$					
$t_{1/2}(s)$	360	450	600					
The order of the reaction is								

(a) 0 (b) 1 (c) 2 (d) 3

29. The CORRECT statement regarding the molecules BF_3 and CH_4 is

- (a) Both BF_3 and CH_4 are microwave active
- (b) Both BF_3 and CH_4 are infrared active IA_{A}
- (c) CH₄ is microwave active and infrared inactive
- (d) BF_3 is microwave active and infrared active
- 30. For the consecutive reaction, $X \xrightarrow{k_X} Y \xrightarrow{k_Y} Z$

 C_0 is the initial concentration of X. The concentration of X, Y and Z at time t are

 C_x , C_y and C_z , respectively. The expression for the concentration Y at time t is

(a)
$$\frac{k_{x}C_{0}}{k_{y}-k_{x}}(e^{-k_{x}t}-e^{-k_{y}t})$$

(b) $\frac{k_{x}C_{x}}{k_{y}-k_{x}}(e^{-k_{x}t}-e^{-k_{y}t})$
(c) $\frac{k_{x}C_{0}}{k_{y}-k_{x}}(e^{-k_{y}t}-e^{-k_{x}t})$
(d) $\frac{k_{x}C_{x}}{k_{y}-k_{x}}(e^{-k_{y}t}-e^{-k_{x}t})$

<u>Attempt ALL the questions. Q.31 – Q.40 Multiple Select Question</u> (MSQ), carry TWO mark each (no negative marks).

- **31.** The **CORRECT** statement(s) about the species is (are)
 - (a) $CpMo(CO)_3$ and $CpW(CO)_3$ are isoelectronic (where Cp is cyclopentadienyl)
 - (b) CH_2^- and NH_2 are isolobal and isoelectronic
 - (c) BH and CH are isolobal and isoelectronic
 - (d) CH_3 and $Mn(CO)_5$ are isolobal
- **32.** The complex(es) that show(s) Jahn-Teller distortion is (are)
 - (a) $[Co(CN)_5(H_2O)]^{3-}$ (b) $[NiF_6]^{2-}$ (c) $[Mn(CNMe)_6]^{2+}$

(d)
$$[Co(en)_2F_2]^+$$

8

- 33. The CORRECT statement(s) about sodium nitroprusside is (are)
 - (a) It is a paramagnetic complex
 - (b) Nitroprusside ion is formed in the brown ring test for nitrates
 - (c) It is used for the detection of S^{2-} in aqueous solution
 - (d) It contains nitrosyl ligand as NO⁺



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38. The functional group(s) in reducing sugar that tests positive with Tollen's reagent is (are)

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(d) Acetal

39. Among the following, the anti-aromatic compound(s) is (are)







(d)

- 40. The CORRECT Maxwell relation(s) derived from the fundamental equations of thermodynamics is (are)
 - (a) $\left(\frac{\partial S}{\partial p}\right)_{T} = -\left(\frac{\partial V}{\partial T}\right)_{p}$ (b) $\left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial p}{\partial T}\right)_{V}$ (c) $\left(\frac{\partial T}{\partial V}\right)_{S} = \left(\frac{\partial p}{\partial S}\right)_{V}$ (d) $\left(\frac{\partial T}{\partial p}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{p}$ <u>Attempt ALL the questions. Q.41 – Q.50 Numerical Answer Type</u> (NAT), carry ONE mark each (no negative marks).
- 41. The total number of optically active isomers of dichloridobis(glycinato)cobaltate (III) ion is_____.
- 42. The total number of microstates possible for a d⁸ electronic configuration is_____.
- 43. For the following fusion reaction, 4 ¹H → ⁴He + 2β⁺ + 2υ + γ
 the *Q*-value (energy of the reaction) in MeV is _____. (rounded off to one decimal place)

(Given: Mass of ¹H nucleus = 1.007825 u; mass of ⁴He nucleus = 4.002604 u)

44. MgO crystallizes as rock salt structure with unit cell length 2.12 Å. From electrostatic model, the calculated lattice energy in kJ mol⁻¹ is _____. (rounded off to the nearest integer)

(Given: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; Madelung constant = 1.748;

 $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$; charge of an electron = $1.602 \times 10^{-19} \text{ C}$)

45. Calcium crystallizes in *fcc* lattice of unit cell length 5.56 Å and density 1.4848 g cm⁻³. The percentage of Schottky defects in the crystal is______. (rounded off to one decimal place)

(Given: Atomic mass of Ca = 40 g mol⁻¹; $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$) Among the following, the total number of terpenes (terpenoids) is_____.



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- 47. A buffer solution is prepared by mixing 0. 3 M NH₃ and 0. 1 M NH₄NO₃. If K_b of NH₃ is 1. 6×10^{-5} at 25 °C, then the pH of the buffer solution at 25 °C is _____. (rounded off to one decimal place)
- 48. The dissociation constant of a weak monoprotic acid is 1.6×10^{-5} and its molar conductance at infinite dilution is 360.5×10^{-4} mho m² mol⁻¹. For 0.01 M solution of this acid, the specific conductance is $n \times 10^{-2}$ mho m⁻¹. The value of n is ______. (rounded off to two decimal place)
- 49. Adsorption of a toxic gas on 1.0 g activated charcoal is 0.75 cm³ both at 2.5 atm, 140 K and at 30.0 atm, 280 K. The isosteric enthalpy for adsorption of the gas in kJ mol⁻¹ is_. (rounded off to two decimal place)(Given: R = 8.314 JK⁻¹mol⁻¹)
- 50. If the root mean square speed of hydrogen gas at a particular temperature is 1900 m s⁻¹, then the root mean square speed of nitrogen gas at the same temperature, in m s⁻¹ is _____. (rounded off to the nearest integer)

(Given: atomic mass of $H = 1 \text{ g mol}^{-1}$; atomic mass of $N = 14 \text{ g mol}^{-1}$) <u>Q.51 - Q.60 Numerical Answer Type (NAT), carry TWO marks each</u> (no negative marks).

- 51. If the crystal field splitting energy of [Co(NH₃)₄]²⁺ is 5900 cm⁻¹, then the magnitude of its crystal field stabilization energy, in kJ mol⁻¹ is_____. (rounded off to one decimal place)
- 52. A salt mixture (1.0 g) contains 25 wt% of MgSO₄ and 75 wt% of M₂SO₄. Aqueous solution of this salt mixture on treating with excess BaCl₂ solution results in the precipitation of 1.49 g of BaSO₄. The atomic mass of M in g mol⁻¹ is _____. (rounded off to two decimal place)

(Given: the atomic masses of Mg, S, O, Ba and Cl are 24.31, 32.06, 16.00, 137.33 and 35.45 g mol⁻¹, respectively)

53. The intensity of a monochromatic visible light is reduced by 90% due to absorption on passing through a 5.0 mM solution of a compound. If the path



length is 4 cm, then the molar extinction coefficient of the compound in $M^{-1}cm^{-1}$ is_____.

- 54. The surface tension (γ) of a solution, prepared by mixing 0.02 mol of an organic acid in 1 L of pure water, is represented as $\gamma^* - \gamma = A \log (1 + Bc)$ γ^* is the surface tension of pure water, A = 0.03 N m⁻¹, B = 50 mol⁻¹ L and c is concentration in mol L⁻¹. The excess concentration of the organic acid at the surface of the liquid, determined by Gibbs adsorption equation at 300 K is $n \times 10^{-6}$ mol m⁻². The value of n is ______. (Rounded off to two decimal places) (Given: R = 8.314 J K⁻¹ mol⁻¹)
- 55. The separation of energy levels in the rotational spectrum of CO is 3.8626 cm⁻¹. The bond length (assume it does not change during rotation) of CO in Å is ______. (Rounded off to two decimal places)

(Given: Planck's constant $h = 6.626 \times 10^{-34} \text{ J s}$; $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; atomic mass of $C = 12 \text{ g mol}^{-1}$; atomic mass of $0 = 16 \text{ g mol}^{-1}$; $c = 3 \times 10^8 \text{ m s}^{-1}$)

56. A dilute solution prepared by dissolving a nonvolatile solute in one liter water shows a depression in freezing point of 0. 186 K. This solute neither dissociates nor associates in water. The boiling point of the solution in K is ______. (Rounded off to three decimal places)

(Given: For pure water, boiling point = 373.15 K; cryoscopic constant = 1.86 K (mol kg⁻¹)⁻¹; ebullioscopic constant = 0.51 K (mol kg⁻¹)⁻¹

57. The thermodynamic data at 298K for the decomposition reaction of limestone at equilibrium is given below

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Thermodynamic quantity	CaCO ₃ (s)	CaO(s)	CO ₂ (g)
μ^0 (kJ mol ⁻¹)	-1128.8	-604.0	-394.4
ΔH_{f}^{0} (kJ mol ⁻¹)	-1206.9	-635.1	-393.5

The partial pressure of $CO_2(g)$ in atm evolved on heating limestone at 1200K is

_____. (Rounded off to two decimal places) (Given: $R = 8.314 JK^{-1} mol^{-1}$)

58. The mean ionic activity coefficient of 0.004 molal CaCl₂ in water at 298 K is _____.
(Rounded off to three decimal places) (Given: Debye-Hückel constant for an aqueous solution at 298 K is 0.509 kg^{1/2} mol^{-1/2})

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59. For the reaction,

$$Q + R \xrightarrow{k_1} X \xrightarrow{k_2} P$$

$$k_1=2.5\times 10^5$$
 L mol^{-1} s^{-1}, $k_{-1}=1.0\times 10^4$ s^{-1} and $k_2=10s^{-1}$

Under steady state approximation, the rate constant for the overall reaction in $L \mod^{-1} s^{-1}$ is_____. (rounded off to the nearest integer)

60. For the molecule, H₃C-CH=CH-CH(OH)-CH=CH-CH=C(CH₃)₂ the number of all possible stereoisomers is _____.

Q.No	Ans		Q.No	Ans		Q.No	Ans
1.	С	1	21.	b	12	41.	6
2.	с	2.	22.	С	15	42.	45
3.	d	IJ.	23.	a	1	43.	26.7 to 26.8
4.	с	SO	24.	d		44.	-7880 to -6150 OR 6150 to 7880
5.	a	Ì	25.	С	2/	45.	3.9 to 4.1
6.	с		26.	С	1	46.	7
7.	b		27.	a		47.	9.7
8.	b		28.	С	K	48.	1.44 to 1.47
9.	b	I,	29.	b		49.	-5.81 to -5.75
10.	а		30.	а		50.	507 to 510
11.	b		31.	a, b, d	E	51.	-84.8 to -84.2 OR 84.2 to 84.8
12.	d		32.	a, c		52.	38.98 to 39.25
13.	с		33.	c, d		53.	50
14.	b		34.	a, c		54.	2.60 to 2.62
15.	с		35.	a, d		55.	1.12 to 1.14
16.	с		36.	a, d		56.	373.201
17.	d		37.	b		57.	4.20 to 4.35
18.	b		38.	a, b, c		58.	0.772 to 0.775
19.	d		39.	b, c, d		59.	250
20.	d		40.	a, b, d		60.	8

Answer Key

Q. 1 – 10	1 Mark			Q. 41 – 50	1 Mark
	(MCQ)				(NAT)
Q. 11 – 30	2 Mark	Q. 31 – 40	2 Mark	Q. 51 – 60	2 Mark
	(MCQ)		(MSQ)		(NAT)



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