PART II-CHEMISTRY

SECTION 1 (Maximum Marks: 24)

This section contains SIX (06) questions.

•Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).

• For each question, choose the correct option(s) to answer the question.

• Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If only (all) the correct option(s) is (are) chosen.

Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.

Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.

Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.

Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).

Negative Marks : -2 In all other cases.

• For Example: If first, third and fourth are the ONLY three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option) without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in -2 marks

Q.1. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$ (en = H₂NCH₂CH₂NH₂) is (are) (A) It has two geometrical isomers

(B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands

(C) It is paramagnetic

(D) It absorbs light at longer wavelength as compared to $[Co(en)(NH_3)_4]^{3+}$



Since (en) and NH₃ are strong field ligand, so it should be diamagnetic complex (D)

 (NH_3) is a stronger ligand than

 H_2O , so, $[Co(en)(NH_3)_4]^{3+}$ should absorb shorter wavelength than $[Co(en)(NH_3)_3(H_2O)]^{3+}$.

Q.2 The correct option(s) to distinguish nitrate salts of Mn²⁺ and Cu²⁺ taken separately is (are)
(A) Mn²⁺ shows the characteristic green colour in the flame test
(B) Only Cu²⁺ shows the formation of precipitate by passing H₂S in acidic medium
(C) Only Mn²⁺ shows the formation of precipitate by passing H₂S in faintly basic medium
(D) Cu²⁺/Cu has higher reduction potential than Mn²⁺/Mn (measured under similar conditions)

Sol. B, D

 \dot{Cu}^{2+} shows the characteristic green colour in the flame test. Ksp of CuS < Ksp of MnS $E^{\circ}_{Cu^{2+}/Cu} > E^{\circ}_{Mn^{2+}/Mn}$

Q.3 Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51%), Q (47%) and R(2%). The major product(s) of the following reaction sequence is (are)







*Q.4. The Fischer presentation of D-glucose is given below



D-glucose

The correct structures(s) of β -L-glucopyranose is(are)





Sol.



Q.5 For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning (t = 0) and at time t are P₀ and P_t, respectively. Initially, only A is present with concentration [A]₀, and t_{1/3} is the time required for the partial pressure of A to reach $1/3^{rd}$ of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases)





$$\begin{split} \Delta G^{0} &= -RT \ln K_{eq}, \ \Delta G^{0} < 0 \\ \frac{\ln K_{T_{1}}}{\ln K_{T_{2}}} > \frac{T_{2}}{T_{1}} > 1 \\ \Rightarrow \frac{K_{T_{1}}}{K_{T_{2}}} > 1 \\ \Rightarrow K_{T_{2}} < K_{T_{1}} (exothermic) \\ \Delta H^{0} < 0, \text{ since (P) at } T_{2} < at T_{1}. \\ \Delta G^{0} &= \Delta H^{0} - T\Delta S^{0} \\ T\Delta S^{0} &= \Delta H^{0} - \Delta G^{0} \\ \Delta S^{0} &= \frac{\Delta H^{0} - \Delta G^{0}}{T}; \ (\Delta H^{0}) > (\Delta G^{0}) \\ \Delta S^{0} < 0 \\ Also, \ -T_{1} \ln K_{T_{1}} < -T_{2} \ln K_{T_{2}} II \\ \Delta G^{0}_{T_{1}} < \Delta G^{0}_{T_{2}} \\ \Delta H^{0}_{T_{1}} - T\Delta S^{0}_{T_{2}} < \Delta H^{0}_{T_{2}} - T\Delta S^{0}_{T_{2}} \\ It is possible only if \Delta S^{0} < 0. \end{split}$$

SECTION 2 (Maximum Marks: 24)

- This section contains EIGHT (08) questions. The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, -0.33, -.30, 30.27, -127.30) using the mouse and the onscreen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme: *Full Marks*: +3 If ONLY the correct numerical value is entered as answer. *Zero Marks*: 0 In all other cases
- Q.7 The total number of compounds having at least one bridging oxo group among the molecules given below is _____. N₂O₃, N₂O₅, P₄O₆, P₄O₇, H₄P₂O₅, H₅P₃O₁₀, H₂S₂O₃, H₂S₂O₅

Sol.

6



 $2H_3PO_3 \longrightarrow H_4P_2O_5 + H_2O_5$



- Q.8 Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O₂ consumed is _____. (Atomic weights in g mol⁻¹: O = 16, S = 32, Pb = 207)
- Sol. 6.47 kg $2PbS+3O_2 \longrightarrow 2PbO+2SO_2$ $2PbO+PbS \longrightarrow 3Pb+SO_2$

 $3PbS + 3O_2 \longrightarrow 3Pb + 3SO_2$ $32kg \qquad 207 kg$ $1 kg \longrightarrow \frac{207}{32} = 6.47 kg$

- *Q.9 To measure the quantity of MnCl₂ dissolved in an aqueous solution, it was completely converted to KMnO₄ using the reaction, MnCl₂ + K₂S₂O₈ + H₂O \rightarrow KMnO₄ + H₂SO₄ + HCl (equation not balanced). Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 mg) was added in portions till the colour of the permanganate ion disappeared. The quantity of MnCl₂ (in mg) present in the initial solution is _____. (Atomic weights in g mol⁻¹: Mn = 55, Cl = 35.5)
- Sol. 126 Number of meq of $MnCl_2 =$ number of meq of $KMnO_4$ = number of meq of $H_2C_2O_4$ = 5

Weight of MnCl₂ taken = $5 \times 10^{-3} \times \frac{126}{5}$ gm = 126 mg



*Q.10 For the given compound **X**, the total number of optically active stereoisomers is _____



Q.11 In the following reaction sequence, the amount of **D** (in g) formed from 10 moles of acetophenone is _____. (Atomic weights in g mol⁻¹: H = 1, C = 12, N = 14, O = 16, Br = 80. The yield (%) corresponding to the product in each step is given in the parenthesis)



Sol.



Amount of (D) = $1.5 \times 330 = 495.0$ g

Q.12 The surface of copper gets tarnished by the formation of copper oxide. N₂ gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the N₂ gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below: $2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$

 $p_{\rm H_2}$ is the minimum partial pressure of $\rm H_2$ (in bar) needed to prevent the oxidation at 1250 K. The value of

 $\ln(p_{H_2})$ is ____

(Given: total pressure = 1 bar, R (universal gas constant) = 8 J K⁻¹ mol⁻¹, $\ln(10) = 2.3$. Cu(s) and Cu₂O(s) are mutually immiscible.

At 1250 K: $2Cu(s) + \frac{1}{2}O_2(g) \rightarrow Cu_2O(s); \Delta G^{\theta} = -78,000 \text{ J mol}^{-1}$ $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g); \Delta G^{\theta} = -1,78,000 \text{ J mol}^{-1}; G \text{ is the Gibbs energy})$

Sol. -14.6

From the given data:

For $2Cu(s) + H_2O(g) \implies Cu_2O(s) + H_2(g)$ $\Delta G^0 = 100000$ Hence $\Delta G^0 = 100000 = -RT \ln Kp$ and $K_P = \frac{P_{H_2}}{P_{H_2O}} (P_{H_2O(g)} = 0.01 \text{ bar})$

On calculating; $\ln P_{H_2} = -14.6$

Q.13 Consider the following reversible reaction,

 $A(g)+B(g) \rightleftharpoons AB(g)$

The activation energy of the backward reaction exceeds that of the forward reaction by 2RT (in J mol⁻¹). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^{θ} (in J mol⁻¹) for the reaction at 300 K is _____. (Given; ln(2) = 0.7, RT = 2500 J mol⁻¹ at 300 K and G is the Gibbs energy)

$$A(g) + B(g) \xrightarrow{} AB(g)$$

$$(E_a)_b - (E_a)_f = 2RT$$

$$\frac{A_f}{A_b} = 4$$

$$\Delta G^{\circ} = -RT \ln K_{eq}$$

$$K_f = A_f e^{-(E_a)_f/RT}$$

$$K_b = A_b e^{-(E_a)_b/RT}$$

$$K_{eq} = \frac{K_f}{K_b} = \frac{A_f}{A_b} \times e^{-\frac{(E_a)_f}{RT}} \times e^{\frac{+(E_a)_b}{RT}} = 4 \times e^{\frac{(E_a)_b - (E_a)_f}{RT}}$$

$$K_{eq} = 4 \times e^2$$

$$\Delta G^{\circ} = -RT \times \ln(4 \times e^2)$$

$$\Delta G^{0} = -RT(\ln 4 + 2\ln e)$$

$$\Delta G^{0} = -RT(1.40 + 2)$$

$$\Delta G^{0} = -RT(3.40)$$

$$\Delta G^{0} = -8500J$$

Q.14 Consider an electrochemical cell: $A(s) | A^{n^+}(aq, 2 M) || B^{2n^+}(aq, 1 M) | B(s)$. The value of ΔH^{θ} for the cell reaction is twice that of ΔG^{θ} at 300 K. If the emf of the cell is zero, the ΔS^{θ} (in J K⁻¹ mol⁻¹) of the cell reaction per mole of B formed at 300 K is _____. (Given: $\ln(2) = 0.7$, R (universal gas constant) = 8.3 J K⁻¹ mol⁻¹. *H*, *S* and *G* are enthalpy, entropy and Gibbs energy, respectively.)

Sol.
$$-11.62 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$A(s) | A^{n+}(aq, 2M) || B^{2n+}(aq, 1M) |B(s)$$

$$2A(s) \longrightarrow 2A^{n+} + 2ne^{-}$$

$$B^{2n+} + 2ne^{-} \longrightarrow B(s)$$

$$2A(s) + B^{2n+} \longrightarrow 2A^{n+} + B(s)$$

$$Q = \left[\frac{A^{n+}}{[B^{2n+}]}^{2} = \frac{2 \times 2}{1} = 4$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta H^{\circ} = 2\Delta G^{\circ}$$

$$E^{0}_{cell} = \frac{RT}{2nF} \ln 4$$

$$\Delta G^{0} = -2n \times F \times \frac{RT}{2nF} \ln 4$$

$$\Delta G^{0} = -RT \ln 4$$

$$\Delta S^{0} = \frac{\Delta H^{0} - \Delta G^{0}}{T} = \frac{\Delta G^{0}}{T} = -\frac{RT \ln 4}{T}$$

$$\Delta S^{0} = -8.314 \times 1.4$$

$$= -11.62 \text{ J mol}^{-1} \text{K}^{-1}$$

SECTION 3 (Maximum Marks: 12)

- This section contains FOUR (04) questions.
- Each question has TWO (02) matching lists: LIST I and LIST II.
- FOUR options are given representing matching of elements from LIST I and LIST II. ONLY ONE of these four options corresponds to a correct matching.
- For each question, choose the option corresponding to the correct matching.
- For each question, marks will be awarded according to the following marking scheme: *Full Marks* : +3 If ONLY the option corresponding to the correct matching is chosen. *Zero Marks* : 0 If none of the options is chosen (i.e. the question is unanswered). *Negative Marks* : -1 In all other cases

Q.15 🛛	Match each set of h	ybrid orbitals from LIS	ST–I with com	plex(es) given	in LIST-II
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LIST-I	LIST-II		
P. dsp^2	1. $[FeF_6]^{4-}$		
\mathbf{Q} . sp ³	2. $[Ti(H_2O)_3Cl_3]$		
R. sp^3d^2	3. $[Cr(NH_3)_6]^{3+}$		
S. d^2sp^3	4. $[FeCl_4]^{2-}$		
	5. Ni(CO) ₄		
	6. $[Ni(CN)_4]^{2-}$		

The correct option is

- (A) $\mathbf{P} \rightarrow 5$; $\mathbf{Q} \rightarrow 4,6$; $\mathbf{R} \rightarrow 2,3$; $\mathbf{S} \rightarrow 1$
- (B) $\mathbf{P} \rightarrow 5,6; \mathbf{Q} \rightarrow 4; \mathbf{R} \rightarrow 3; \mathbf{S} \rightarrow 1,2$
- (C) $\mathbf{P} \rightarrow 6$; $\mathbf{Q} \rightarrow 4,5$; $\mathbf{R} \rightarrow 1$; $\mathbf{S} \rightarrow 2,3$
- (D) $\mathbf{P} \rightarrow 4,6; \mathbf{Q} \rightarrow 5,6; \mathbf{R} \rightarrow 1,2; \mathbf{S} \rightarrow 3$

C $dsp^{2}: [Ni(CN)_{4}]^{2^{-}}$ $sp^{3}: [FeCl_{4}]^{2^{-}}; [Ni(CO)_{4}]$ $sp^{3}d^{2}: [FeF_{6}]^{4^{-}}$ $d^{2}sp^{3}: [Ti(H_{2}O)_{3} Cl_{3}], [Cr(NH_{3})_{6}]^{3^{+}}$

Q.16 The desired product **X** can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II.

(Given, order of migratory aptitude: aryl > alkyl > hydrogen)





The correct option is

- (A) $\mathbf{P} \rightarrow 1$; $\mathbf{Q} \rightarrow 2,3$; $\mathbf{R} \rightarrow 1,4$; $\mathbf{S} \rightarrow 2,4$
- (B) $\mathbf{P} \rightarrow 1,5; \mathbf{Q} \rightarrow 3,4; \mathbf{R} \rightarrow 4,5; \mathbf{S} \rightarrow 3$
- (C) $\mathbf{P} \rightarrow 1,5; \mathbf{Q} \rightarrow 3,4; \mathbf{R} \rightarrow 5; \mathbf{S} \rightarrow 2,4$
- (D) $\mathbf{P} \rightarrow 1,5; \mathbf{Q} \rightarrow 2,3; \mathbf{R} \rightarrow 1,5; \mathbf{S} \rightarrow 2,3$

Sol.



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Q.17 LIST-I contains reactions and LIST-II contains major products.

Match each reaction in LIST-I with one or more products in LIST-II and choose the correct option. (A) $\mathbf{P} \rightarrow 1,5$; $\mathbf{Q} \rightarrow 2$; $\mathbf{R} \rightarrow 3$; $\mathbf{S} \rightarrow 4$ (B) $\mathbf{P} \rightarrow 1,4$; $\mathbf{Q} \rightarrow 2$; $\mathbf{R} \rightarrow 4$; $\mathbf{S} \rightarrow 3$ (C) $\mathbf{P} \rightarrow 1,4$; $\mathbf{Q} \rightarrow 1,2$; $\mathbf{R} \rightarrow 3,4$; $\mathbf{S} \rightarrow 4$ (D) $\mathbf{P} \rightarrow 4,5$; $\mathbf{Q} \rightarrow 4$; $\mathbf{R} \rightarrow 4$; $\mathbf{S} \rightarrow 3,4$



*Q.18 Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solutions on [H⁺] are given in LIST-II.

(Note: Degree of dissociation (α) of weak acid and weak base is << 1; degree of hydrolysis of salt <<1; [H⁺] represents the concentration of H⁺ ions)

	LIST-I	LIST-II
Р.	(10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid)	1. the value of $[H^+]$ does not change
	diluted to 60 mL	on dilution
Q .	(20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid)	2. the value of $[H^+]$ changes to half of its
	diluted to 80 mL	initial value on dilution
R.	(20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia	3. the value of $[H^+]$ changes to two times
	solution) diluted to 80 mL	of its initial value on dilution
S.	10 mL saturated solution of Ni(OH) ₂ in equilibrium with excess solid Ni(OH) ₂ is diluted to 20 mL (solid Ni(OH)) is diluted to 20 mL (solid Ni(OH)).	4. the value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times
	$NI(OH)_2$ is still present after dilution).	of its initial value on dilution
		5. the value of $[H^+]$ changes to $\sqrt{2}$ times of
		its initial value on dilution

Match each process given in LIST-I with one or more effect(s) in LIST-II. The correct option is

(A) $\mathbf{P} \rightarrow 4$; $\mathbf{Q} \rightarrow 2$; $\mathbf{R} \rightarrow 3$; $\mathbf{S} \rightarrow 1$ (B) $\mathbf{P} \rightarrow 4$; $\mathbf{Q} \rightarrow 3$; $\mathbf{R} \rightarrow 2$; $\mathbf{S} \rightarrow 3$ (C) $\mathbf{P} \rightarrow 1$; $\mathbf{Q} \rightarrow 4$; $\mathbf{R} \rightarrow 5$; $\mathbf{S} \rightarrow 3$ (D) $\mathbf{P} \rightarrow 1$; $\mathbf{Q} \rightarrow 5$; $\mathbf{R} \rightarrow 4$; $\mathbf{S} \rightarrow 1$

Sol.

D

$$\frac{\mathbf{K}_{w}}{\mathbf{K}_{a}} = \frac{\left[\mathbf{CH}_{3}\mathbf{COO^{-}}\right]\left[\mathbf{OH}^{-}\right]}{\left[\mathbf{CH}_{3}\mathbf{COOH}\right]}$$
$$\left[\mathbf{OH}^{-}\right] = \left(\frac{\mathbf{K}_{w}}{\mathbf{K}_{a}} \times \mathbf{C}\right)^{1/2}$$

(P) is a buffer, so [H⁺] does not change on dilution, as [salt] = [acid].
(Q) contains only CH₃COONa

So $CH_3COO^- + H_2O \Longrightarrow CH_3COOH + OH^-$

$$\left[OH^{-} \right] = \sqrt{K_{h} \times C} \Rightarrow \left[H^{+} \right]$$
 decreases by $\sqrt{2}$ times

So, $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

$$\left[\mathrm{H}^{+}\right] = \sqrt{\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{K}_{\mathrm{b}}} \times \mathrm{C}}$$

So, C is made
$$\frac{1}{2}$$
 so, [H⁺] becomes $\frac{1}{\sqrt{2}}$

(S) it is a solubility equilibria So dilution does not effect $[H^+]$ or $[OH^-]$