Chemistry

SECTION 1 (Maximum Marks: 12)

- This section contains **FOUR (04)** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	: +3	If **ONLY** the correct option 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.

1. The heating of NH_4NO_2 at $60-70^{\circ}C$ and NH_4NO_3 at $200-250^{\circ}C$ is associated with the formation of nitrogen containing compounds **X** and **Y**, respectively. **X** and **Y**, respectively, are

(A) N_2 and N_2O

(B) NH_3 and NO_2

(C) NO and N_2O

(D) N_2 and NH_3

Ans. (A)

Sol. $NH_4NO_2 \xrightarrow{60^{\circ}-70^{\circ}C} N_2 + H_2O$

$NH_4NO_3 \xrightarrow{200^{\circ}-250^{\circ}C} N_2O + H_2O$

2. The correct order of the wavelength maxima of the absorption band in the ultraviolet-visible region for the given complexes is

(A) $[Co(CN)_6]^{3-} < [Co(NH_3)_6]^{3+} < [Co(NH_3)_5(H_2O)]^{3+} < [Co(NH_3)_5(Cl)]^{2+}$

(B) $[Co(NH_3)_5(Cl)]^{2+} < [Co(NH_3)_5(H_2O)]^{3+} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$

(C) $[Co(CN)_6]^{3-} < [Co(NH_3)_5(Cl)]^{2+} < [Co(NH_3)_5(H_2O)]^{3+} < [Co(NH_3)_6]^{3+}$

(D) $[Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-} < [Co(NH_3)_5(Cl)]^{2+} < [Co(NH_3)_5(H_2O)]^{3+}$

Ans. (A)

Sol. Stength of ligand $CN^- > NH_3 > NH_3, H_2O > NH_3, Cl$

Splitting	>	>	>
Energy absob	>	>	>
λ_{absorb}	<	<	<

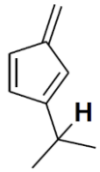
3. One of the products formed from the reaction of permanganate ion with iodide ion in neutral aqueous medium is

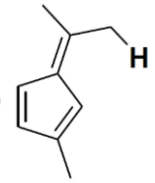
(A) I_2 (B) 10_3^- (C) 10_4^- (D) IO_2^-

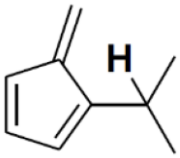
Ans. (B)

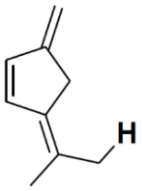
Sol. $MnO_4^- + I^- \xrightarrow[\text{medium}]{\text{Neutral}} MnO_2 + IO_3^-$

4. Consider the depicted hydrogen (H) in the hydrocarbons given below. The most acidic hydrogen (H) is

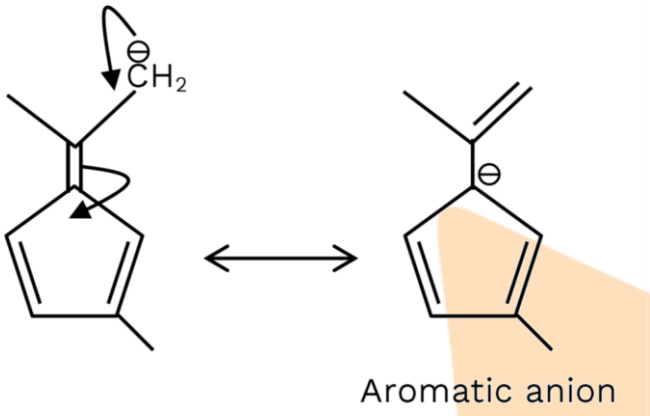
(A) 

(B) 

(C) 

(D) 

Ans. (B)

Sol. 

Aromatic anion

SECTION 2 (Maximum Marks: 12)

- This section contains **THREE (03)** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONE OR MORE THAN ONE** of these four option(s) is(are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	: +4	**ONLY** if (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;
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, in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answers, then
  choosing ONLY (A), (B) and (D) will get +4 marks;
  choosing ONLY (A) and (B) will get +2 marks;
  choosing ONLY (A) and (D) will get +2 marks;
  choosing ONLY (B) and (D) will get +2 marks;
  choosing ONLY(A) will get +1 mark;
  choosing ONLY (B) will get +1 mark;
  choosing ONLY (D) will get +1 mark;
  choosing no option (i.e. the question is unanswered) will get 0 marks; and choosing any other combination of options will get -2 marks.

5. Regarding the molecular orbital (MO) energy levels for homonuclear diatomic molecules, the INCORRECT statement(s) is(are)

(A) Bond order of Ne_2 is zero.

(B) The highest occupied molecular orbital (HOMO) of F_2 is σ-type.

(C) Bond energy of O_2^+ is smaller than the bond energy of O_2.

(D) Bond length of Li_2 is larger than the bond length of B_2.

Ans. (BC)

Sol. (A) True, $BO = \frac{1}{2}$ [Number of e^- in BMO − Number of e^- in ABMO]

(B) HOMO $\Rightarrow F_2 \Rightarrow \sigma$ (false) it's π_{ABMO}

(C) BO of $O_2^+ = 2.5$ and $O_2 = 2$

B.E. of $O_2^+ > O_2$ but given B.E. of $O_2^+ < O_2$ (False)

(D) Li_2, $B_2 = BO = 1$

Li > Be > B

Zeff ↑ Size ↓ (Bond length decreases)

$Li_2 > B_2$ (Bond length) (True)

6. The pair(s) of diamagnetic ions is(are)

(A) La^{3+}, Ce^{4+}

(B) Yb^{2+}, Lu^{3+}

(C) La^{2+}, Ce^{3+}

(D) Yb^{3+}, Lu^{2+}

Ans. (AB)

Sol. Diamagnetic $\Rightarrow$ Species having paired electron & weakly repel magnetic field ℓ in

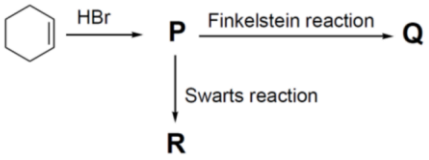
$_{57}La^{+3} =$ $[Xe]6\,s^0 5\,d^0 \Rightarrow La^{+3} \Rightarrow$ Dia magnetic

$_{58}Ce^{+4} =$ $[Xe]6\,s^0 4f^0 5\,d^0 \Rightarrow$ Dia magnetic

$_{70}Yb^{+2} =$ $[Xe]6\,s^0 4f^{14} \Rightarrow$ Dia magnetic

$_{71}Lu^{3+} =$ $[Xe]6\,s^0 4f^{14} 5\,d^0 \Rightarrow$ Dia magnetic

7. F or the reaction sequence given below, the correct statement(s) is (are)



(In the options, X is any atom other than carbon and hydrogen, and it is different in P,Q and R)

(A) C – X bond length in P,Q and R follows the order Q > R > P.

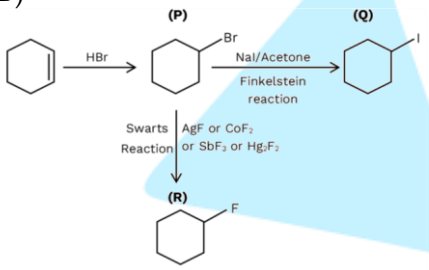
(B) C – X bond enthalpy in P,Q and R follows the order R > P > Q.

(C) Relative reactivity toward S_N2 reaction in P,Q and R follows the order P > R > Q.

(D) pK_a value of the conjugate acids of the leaving groups in P,Q and R follows the order R > Q > P.

Ans. (B)

Sol.



(1) C – X bond length order is Q > P > R

(2) C – X bond enthalpy orde is R > P > Q

(3) S_N2 reactivity order is Q > P > R

(4) pK_a value order is R > P > Q

8. In an electrochemical cell, dichromate ions in aqueous acidic medium are reduced to Cr^{3+}. The current (in amperes) that flows through the cell for 48.25 minutes to produce 1 mole of Cr^{3+} is_____.

Use: 1 Faraday $= 96500 Cmol^{-1}$

Ans. (100)

Sol. $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

Mole of electrons used $= \frac{i \times t}{f} = \frac{48.25 \times 60 \times i}{96500}$

$= \frac{6}{2} \times$ mole of Cr^{3+} formed

$i = \frac{96500 \times 3}{48.25 \times 60} = 100 amp.$

SECTION 3 (Maximum Marks: 24)

- This section contains SIX (06) questions.
- The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value of the answer using the mouse and the onscreen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, truncate/roundoff the value to TWO decimal places.
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 ONLY if the correct numerical value is entered;
  Zero Marks : 0 In all other cases.

9. At $25^{\circ}C$, the concentration of H^+ ions in $1.00\times10^{-3}M$ aqueous solution of a weak monobasic acid having acid dissociation constant (K_a) of 4.00×10^{-11} is $\mathbf{X}\times10^{-7}M$. The value of **X** is .

Use: Ionic product of water $(K_w)=1.00\times10^{-14}$ at $25^{\circ}C$

Ans. (2.24)

Sol.

$$HA \rightleftharpoons H^+ + A^-$$

$t=0$ C

t_{eq} $C(1-a)$ $(Ca+x)$ Ca

equation of water

$$H_2O \rightleftharpoons H^+ + OH^-$$

$(x+c\alpha)$ x

$$K_w=[H^+][OH^-]=[H^+]x$$

$$\text{Now } K_aC+K_w=[H^+](C\alpha+x)=[H^+]^2$$

$$[H^+]=\sqrt{K_aC+K_w}$$

$$=\sqrt{\left(4\times10^{-11}\times10^{-3}\right)+10^{-14}}$$

$$=\sqrt{5}\times10^{-7}M=x\times10^{-7}\ m$$

$$x=2.24$$

10. Molar volume (V_m) of a van der Waals gas can be calculated by expressing the van der Waals equation as a cubic equation with V_m as the variable. The ratio (in moldm $^{-3}$) of the coefficient of V_m^2 to the coefficient of V_m for a gas having van der Waals constants $a=6.0dm^6$ atm mol^{-2} and $b=0.060dm^3\ mol^{-1}$ at 300 K and 300 atm is

Use: Universal gas constant $(R)=0.082dm^3atmmol^{-1}\ K^{-1}$

Ans. (-7.1)

Sol. $\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT$

Cubic from

$PV_m^3-(bP+RT)V_m^2+aV_m-ab=0$

Coefficient of $V_m^2=(bP+RT)$

Coefficient of $V_m=a$

$\therefore -\frac{(bP+RT)}{a}=-\frac{(0.06\times 300)+(0.082\times 300)}{6}$

$=-\frac{18+24.6}{6}=-7.1$

11. Considering ideal gas behavior, the expansion work done (in kJ) when 144 g of water is electrolyzed completely under constant pressure at 300 K is_____.

Use: Universal gas constant $(R)=8.3\ J\ K^{-1}\ mol^{-1}$; Atomic mass (in amu): $H=1, O=16$

Ans. (-29.88 kJ)

Sol. $2H_2O(\ell)\rightarrow 2H_2(g)+O_2(g)$

mole of water electro lysed $=\frac{144}{18}=8$

$\therefore$ mole of gases formed $(H_2+O_2)=8+4=12$

Work done $=-\Delta n_{gas}RT$

$=-12\times 8.3\times 300\ J$

$=-29880\ J$

$=-29.88\ kJ$

$=-29.88\ kJ$

12. The monomer (X) involved in the synthesis of Nylon 6,6 gives positive carbylamine test. If 10 moles of **X** are analyzed using Dumas method, the amount (in grams) of nitrogen gas evolved is_____.

Use: Atomic mass of N (in amu) = 14

Ans. (280)

Sol. $HOOC-(CH_2)_4-COOH+H_2\ N-(CH_2)_6-NH_2\rightarrow$ Nylone –6,6

Adipic acid — Hexamethylene diamine

(x)

(10 mole)

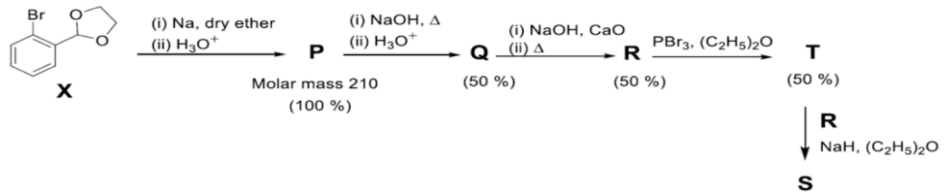
↓ Dumas method

N_2 (gas)

Mol of N_2 evolved in Duma method $=10$

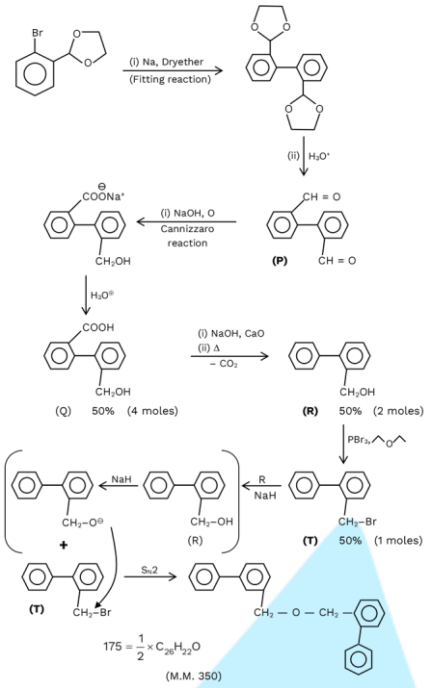
Mass of N_2 gas $=28\times 10=280gm$

13. The reaction sequence given below is carried out with 16 moles of X . The yield of the major product in each step is given below the product in parentheses. The amount (in grams) of S produced is_____.



Ans. (175)

Sol.



SECTION 4 (Maximum Marks: 12)

- This section contains THREE (03) Matching List Sets.
- Each set has ONE Multiple Choice Question.
- Each set has TWO lists: List-I and List-II.
- List-I has Four entries (P), (Q), (R) and (S) and List-II has Five entries (1), (2), (3), (4) and (5).
- FOUR options are given in each Multiple Choice Question based on List-I and List-II and ONLY ONE of these four options satisfies the condition asked in the Multiple Choice Question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 ONLY if the option corresponding to the correct combination 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.

14. The correct match of the group reagents in List-I for precipitating the metal ion given in List-II from solutions, is

List-I	**List-II**
(P) Passing H_2S in the presence of NH_4OH	(1) Cu^{2+}
(Q) $(NH_4)_2CO_3$ in the presence of NH_4OH	(2) Al^{3+}
(R) NH_4OH in the presence of NH_4Cl	(3) Mn^{2+}
(S) Passing H_2S in the presence of dilute HCl	(4) Ba^{2+}
	(5) Mg^{2+}

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

Ans. (A)

Sol. (P) Passing H_2S in presence of NH_4OH

$[S^2]$ is high, it will ppt Group-IV cation. Hence Mn^{+2} ppt as $MnS\downarrow$

(Q) $(NH_4)_2CO_3$ in presence of $NH_4OH \rightarrow 4$

$[OH^-]$ will be low Due to common ion effect, group-V cation ppt. Hence $Ba(OH)_2\downarrow$ ppt

(R) NH_4OH in presence of NH_4Cl group III cation ppt. Hence $Al(OH)_3$ ppt

(S) Passing H_2S in presence of $HCl[S^2]$ is low, group III cation ppt. Hence $Cus\downarrow$

15. The major products obtained from the reactions in List-II are the reactants for the named reactions mentioned in List-I. Match each entry in List-I with the appropriate entry in List-II and choose the correct option.

List-I	**List-II**
(P) Stephen reaction	(1) Toluene $\xrightarrow[(ii)H_3O^+]{(i)CrO_2Cl_2/CS_2}$
(Q) Sandmeyer reaction	(2) Benzoic acid $\xrightarrow[(iii)P_4O_{10},\Delta]{(i)PCl_5\ (ii)NH_3}$
(R) Hoffmann bromamide degradation reaction	(3) Nitrobenzene $\xrightarrow[(273-278K),H_2O]{(i)Fe,HCl\ (ii)HCl,NaNO_2}$
(S) Cannizzaro reaction	(4) Toluene $\xrightarrow[(iii)SO_2Cl_2\ (iv)NH_3]{(i)Cl_2/hv,H_2O\ (ii)Tollen'sreagent}$
	(5) Aniline $\xrightarrow[(iii)aq.NaOH]{(i)(CH_3CO)_2O,Pyridine\ (ii)HNO_3,H_2SO_4,288K}$

(A) $P \to 2; Q \to 4; R \to 1; S \to 3$

(B) $P \to 2; Q \to 3; R \to 4; S \to 1$

(C) $P \to 5; Q \to 3; R \to 4; S \to 2$

(D) $P \to 5; Q \to 4; R \to 2; S \to 1$

Ans. (B)

Sol.

(1) CH_3 → (i) CrO_2Cl_2/CS_2 (ii) $H_3O^{\oplus}$ → $CH=O$ (Reactant for cannizzaro reaction)

(2) $COOH$ → (i) PCl_5 → $C(=O)-Cl$ → (ii) NH_3 → $C(=O)-NH_2$ → (iii) P_4O_{10}, Δ → $C\equiv NH_2$ (Reactant for stephen reaction)

(3) NO_2 → (i) Fe/HCl → NO_2 → (i) HCl, $NaNO_2$ 273–278K, H_2O → $N_2^+Cl^-$ Reaction for sandmeyer reaction

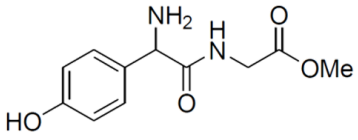
(4) → (i) Cl_2/hv, H_2O → $CH=O$ → (ii) Tollens reagent → $COOH$ → (iii) SO_2Cl_2 → $C(=O)-Cl$ → (iv) NH_3 → $C(=O)-NH_2$ (Reaction for Hoffmann bromamide degradation reaction)

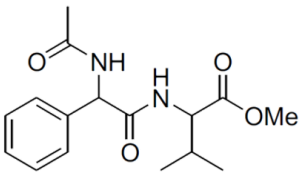
(5) NH_2 → (Pyridine) → $NH-C(=O)-CH_3$ → HNO_3, H_2SO_4, 288K → $NH-C(=O)-CH_3$, NO_2 → aq. NaOH → NH_2, NH_2

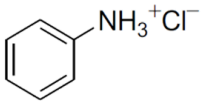
P→2, Q→3, R→4, S→1

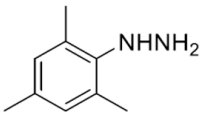
16. Match the compounds in List-I with the appropriate observations in List-II and choose the correct option.

List-I

(P) 

(Q) 

(R) 

(S) 

List-II

(1) Reaction with phenyl diazonium salt gives yellow dye.

(2) Reaction with ninhydrin gives purple color and it also reacts with $FeCl_3$ to give violet color.

(3) Reaction with glucose will give corresponding hydrazone.

(4) Lassiagne extract of the compound treated with dilute HCl followed by addition of aqueous $FeCl_3$ gives blood red color.

(5) After complete hydrolysis, it will give ninhydrin test and it DOES NOT give positive phthalein dye test.

(A) $P \rightarrow 1; Q \rightarrow 5; R \rightarrow 4; S \rightarrow 2$

(B) $P \rightarrow 2; Q \rightarrow 5; R \rightarrow 1; S \rightarrow 3$

(C) $P \rightarrow 5; Q \rightarrow 2; R \rightarrow 1; S \rightarrow 4$

(D) $P \rightarrow 2; Q \rightarrow 1; R \rightarrow 5; S \rightarrow 3$

Ans. (B)

Sol.