PART-II : CHEMISTRY

SECTION – 1 (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 of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +3 **ONLY** if the correct numerical value is entered;

Zero Marks : 0 In all other cases.

1. 2 mol of Hg(g) is combusted in a fixed volume bomb calorimeter with excess of O_2 at 298 K and 1 atm into HgO(s). During the reaction, temperature increases from 298.0 K to 312.8 K. If heat capacity of the bomb calorimeter and enthalpy of formation of Hg(g) are 20.00 kJ K^{-1} and 61.32 kJ mol^{-1} at 298 K, respectively, the calculated standard molar enthalpy of formation of HgO(s) at 298 K is X kJ mol^{-1}. The value of |X| is _____.

[Given: Gas constant R = 8.3 J K^{-1} mol^{-1}]

Answer (90.39)

Sol. $2Hg(g) + O_2(g) \longrightarrow 2HgO(s)$

Heat capacity of calorimeter = 20 kJ K^{-1}

Rise in temperature = 14.8 K

Heat evolved = 20 × 14.8 = 296 kJ

$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$

$= -296 - 3 \times 8.3 \times 298 \times 10^{-3}$

$\simeq -303.42$ kJ

$$\Delta H^\circ = \Delta H_f^o(HgO(s)) - \Delta H_f^o(Hg(g))$$

$$-303.42 = \Delta H_f^o(HgO(s)) - 2 \times 61.32$$

$$\Delta H_f^o(HgO(s)) = -303.42 + 122.64$$

$= -180.78$ kJ

$$|\Delta H_f^o(HgO(s))| = 90.39 \text{ kJ mol}^{-1}$$

2. The reduction potential (E^0, in V) of $MnO_4^-(aq)/Mn(s)$ is _____.

[Given: $E^0_{(MnO_4^-(aq)/MnO_2(s))} = 1.68$ V; $E^0_{(MnO_2(s)/Mn^{2+}(aq))} = 1.21$ V; $E^0_{(Mn^{2+}(aq)/Mn(s))} = -1.03$ V]

Answer (0.77)

Sol. (1) $MnO_4^-(aq) + 4H^+ + 3e \longrightarrow MnO_2(s) + 2H_2O$; $E^\circ = 1.68$ V

$$\Delta G_1^o = -3F(1.68) = -5.04\ F$$

(2) $MnO_2(s) + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O$; $E^\circ = 1.21$ V

$\Delta G_2^\circ = -2F\,(1.21) = -2.42$ F

(3) $Mn^{2+}(aq) + 2e \longrightarrow Mn(s)$; $E^\circ = -1.03$ V

$\Delta G_3^\circ = -2F\,(-1.03) = +2.06$ F

Adding (1), (2) and (3),

$MnO_4^-(aq) + 8H^+ + 7e \longrightarrow Mn(s) + 4H_2O$

$\Delta G = \Delta G_1^\circ + \Delta G_2^\circ + \Delta G_3^\circ$

$= (-5.04 - 2.42 + 2.06)$ F

$-7F\,E^\circ = -5.4F$

$E^\circ = 0.77$ V

3. A solution is prepared by mixing 0.01 mol each of H_2CO_3, $NaHCO_3$, Na_2CO_3, and NaOH in 100 mL of water. pH of the resulting solution is _____.

[Given: pK_{a_1} and pK_{a_2} of H_2CO_3 are 6.37 and 10.32, respectively; log2 = 0.30]

Answer (10.02)

Sol. First acid base reaction between H_2CO_3 and NaOH takes place.

$$\underset{\substack{0.01\text{ mole}\\-}}{H_2CO_3} + \underset{\substack{0.01\text{ mole}\\-}}{NaOH} \longrightarrow \underset{\substack{-\\0.01\text{ mole}}}{NaHCO_3} + \underset{-}{H_2O}$$

In the final solution, we have 0.01 mole Na_2CO_3 and 0.02 moles of $NaHCO_3$.

Here, we have a buffer of $NaHCO_3$ and Na_2CO_3.

$\therefore \quad pH = pK_{a_2} + \log\dfrac{[Salt]}{[Acid]}$

$$= 10.32 + \log\frac{\left(\frac{0.01}{0.1}\right)}{\left(\frac{0.02}{0.1}\right)}$$

$$= 10.32 + \log\frac{1}{2}$$

$= 10.32 - \log 2$

$= 10.32 - 0.3$

$= 10.02$

$\therefore$ pH = 10.02

4. The treatment of an aqueous solution of 3.74 g of $Cu(NO_3)_2$ with excess KI results in a brown solution along with the formation of a precipitate. Passing H_2S through this brown solution gives another precipitate **X**. The amount of **X** (in g) is _____.

[Given: Atomic mass of H = 1, N = 14, O = 16, S = 32, K = 39, Cu = 63, I = 127]

Answer (1.58)

Sol. Number of moles of $Cu(NO_3)_2 = \frac{3.74}{187} = 0.02$

$$2Cu(NO_3)_2 + 4KI \rightarrow Cu_2I_2 \downarrow + I_2 + 4KNO_3$$

Number of moles of Cu_2I_2 precipitated = 0.01

$$Cu_2I_2 + H_2S \rightarrow Cu_2S \downarrow + 2HI$$

Number of moles of Cu_2S precipitated = 0.01

Mass of Cu_2S precipitates = (0.01 × 158) g

= 1.58 g

5. Dissolving 1.24 g of white phosphorous in boiling NaOH solution in an inert atmosphere gives a gas **Q**. The amount of $CuSO_4$ (in g) required to completely consume the gas **Q** is _____.

[Given: Atomic mass of H = 1, O = 16, Na = 23, P = 31, S = 32, Cu = 63]

Answer (2.38)

Sol. $\underset{\substack{1.24\text{ g}\\ \text{or}\\ 0.01\text{ mole}}}{P_4} + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

As NaOH is present in excess. So, amount of phosphine formed is 0.01 mole (as P_4 is limiting)

$$\underset{0.01\text{ mole}}{2PH_3} + 3CuSO_4 \rightarrow Cu_3P_2 + 3H_2SO_4$$

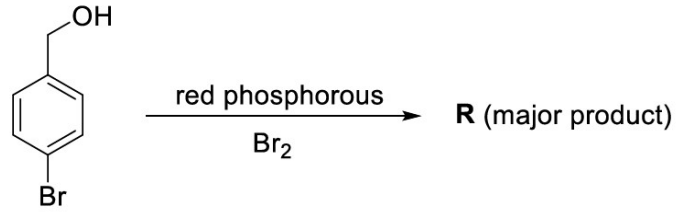
Amount of $CuSO_4$ required = $\frac{3 \times 0.01}{2}$ mole

Mass of $CuSO_4$ (in g) required $= \frac{0.03}{2} \times (63 + 32 + 16 \times 4)$

$$= \frac{0.03}{2} \times 159$$

= 2.38 g

6. Consider the following reaction.

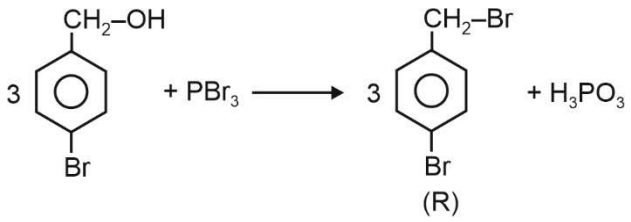


On estimation of bromine in 1.00 g of **R** using Carius method, the amount of AgBr formed (in g) is _____.

[Given: Atomic mass of H = 1, C = 12, O = 16, P = 31, Br = 80, Ag = 108]

Answer (01.50)

Sol. $2P + 3Br_2 \rightarrow 2PBr_3$

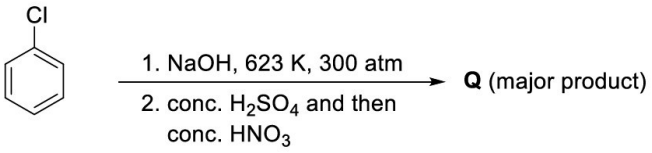


Number of moles in 1 gm of (R) = $\frac{1}{250}$

Number of moles of AgBr formed from (R) = $\frac{2}{250}$

Mass of AgBr formed = $\frac{2\times188}{250} = 1.50$ gm

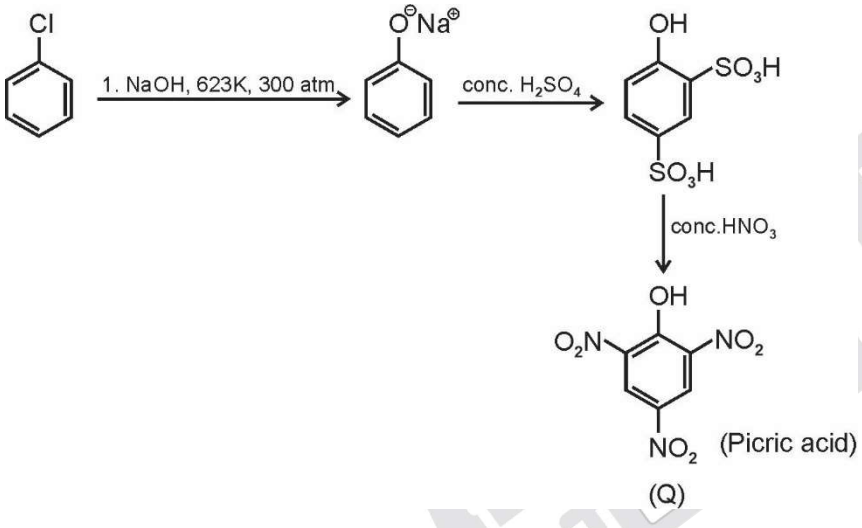
7. The weight percentage of hydrogen in **Q**, formed in the following reaction sequence, is _____.



[Given: Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35]

Answer (1.31)

Sol.



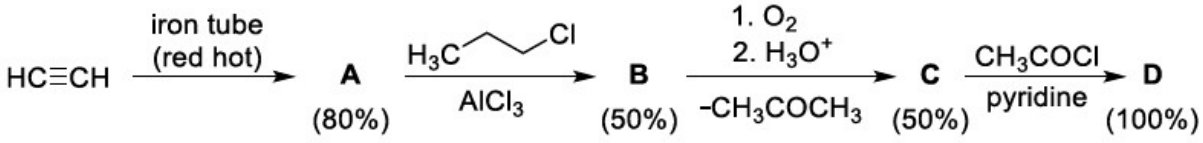
Formula of compound = $C_6H_3N_3O_7$

Molar Mass of compound = (12 × 6 + 3 + 14 × 3 + 16 × 7) g

= 229 g

Weight % of H = $\frac{3}{229}\times100 = 1.31$

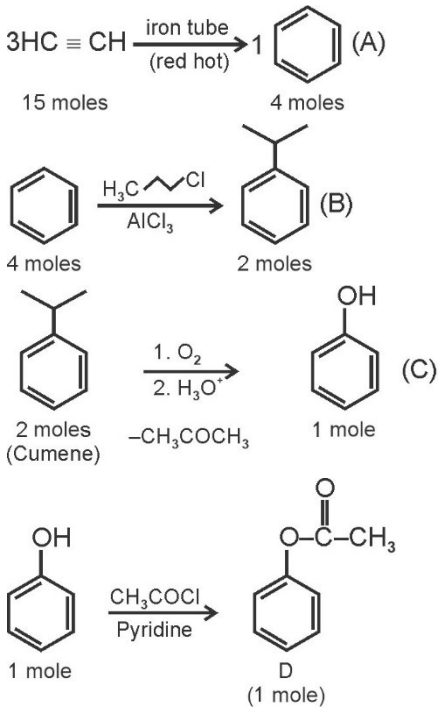
8. If the reaction sequence given below is carried out with 15 moles of acetylene, the amount of the product **D** formed (in g) is _____.



The yields of **A**, **B**, **C** and **D** are given in parentheses.

[Given: Atomic mass of H = 1, C = 12, O = 16, Cl = 35]

Answer (136.00)

Sol. 

Molecular formula of D is $C_8H_8O_2$

Molar mass of D is $(12 \times 8 + 8 \times 1 + 16 \times 2) = 136$ g

$\therefore$ Mass of D is 136

SECTION – 2 (Maximum marks : 24)

- This section contains **SIX (06)** 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.

9. For diatomic molecules, the correct statement(s) about the molecular orbitals formed by the overlap of two $2p_z$ orbitals is(are)

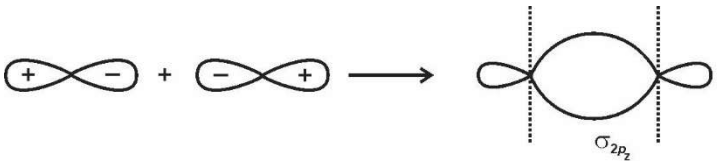
(A) σ orbital has a total of two nodal planes.

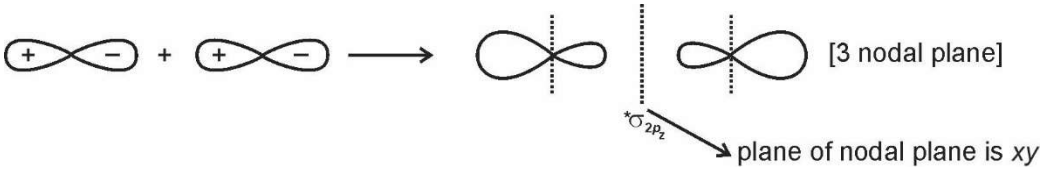
(B) σ^* orbital has one node in the xz-plane containing the molecular axis.

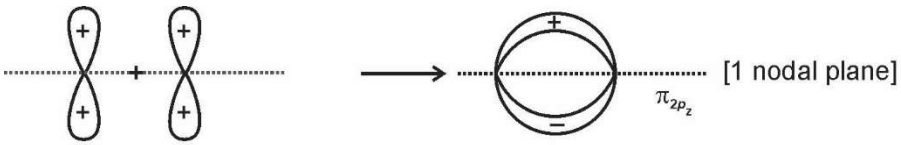
(C) π orbital has one node in the plane which is perpendicular to the molecular axis and goes through the center of the molecule.

(D) π^* orbital has one node in the xy-plane containing the molecular axis.

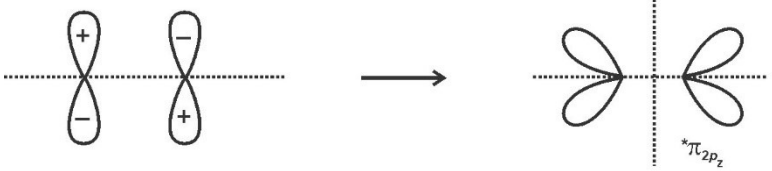
Answer (A, D)

Sol. (A) 

(B) 

(C) 

plane of nodal plane is *xy* plane which is parallel to molecular axis

(D) 

It has two nodal plane and its one nodal plane is in the xy-plane containing the molecular axis

10. The correct option(s) related to adsorption processes is(are)

(A) Chemisorption results in a unimolecular layer.

(B) The enthalpy change during physisorption is in the range of 100 to 140 kJ mol^{-1}.

(C) Chemisorption is an endothermic process.

(D) Lowering the temperature favours physisorption processes.

Answer (A, D)

Sol. (A) First statement is correct as chemisorption results in a unimolecular layer and physisorption result in a multimolecular layer.

(B) Second statement is incorrect as enthalpy change during physisorption is of the range of (20 – 40) kJ mol^{-1}.

(C) Chemisorption is an exothermic process with (80 – 240) kJ mol^{-1} as the enthalpy of adsorption.

(D) Lowering the temperature results in increase in the extent of physisorption.

Hence (A) and (D) are correct.

11. The electrochemical extraction of aluminium from bauxite ore involves

(A) the reaction of Al_2O_3 with coke (C) at a temperature > 2500°C.

(B) the neutralization of aluminate solution by passing CO_2 gas to precipitate hydrated alumina ($Al_2O_3.3H_2O$).

(C) the dissolution of Al_2O_3 in hot aqueous NaOH.

(D) the electrolysis of Al_2O_3 mixed with Na_3AlF_6 to give Al and CO_2.

Answer (B, D)

Sol. (A) The reduction of Al_2O_3 with coke (C) at a temperature > 2500°C is not carried out due to the formation of carbides.

(B) It is correct as neutralisation of aluminate solution is done by passing CO_2 gas to precipitate hydrated alumina.

(C) Reaction of powdered one is carried out with hot concentrated NaOH at 473 K – 523 K and 35 – 36 bar pressure. As pressure conditions are not mentioned, this statement is not absolutely correct.

(D) Electrolysis of Al_2O_3 is done mixed with Na_3AlF_6 to produce Al and CO_2. It is a correct statement.

12. The treatment of galena with HNO_3 produces a gas that is

(A) paramagnetic (B) bent in geometry

(C) an acidic oxide (D) colorless

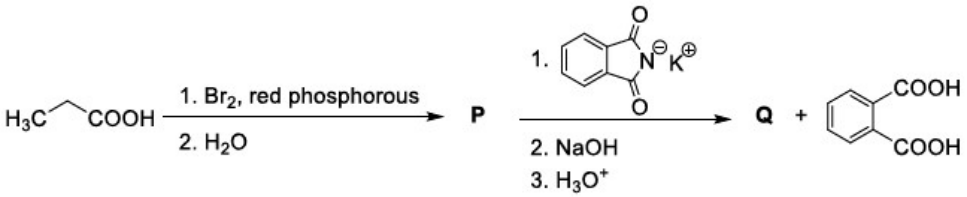
Answer (A, D)

Sol. $PbS + \text{dil. } HNO_3 \rightarrow Pb(NO_3)_2 + S + NO + H_2O$

NO is paramagnetic due to the presence of unpaired electron. It is a neutral oxide. It is colourless.

Hence, (A) and (D) are correct statements.

13. Considering the reaction sequence given below, the correct statement(s) is(are)



(A) **P** can be reduced to a primary alcohol using $NaBH_4$.

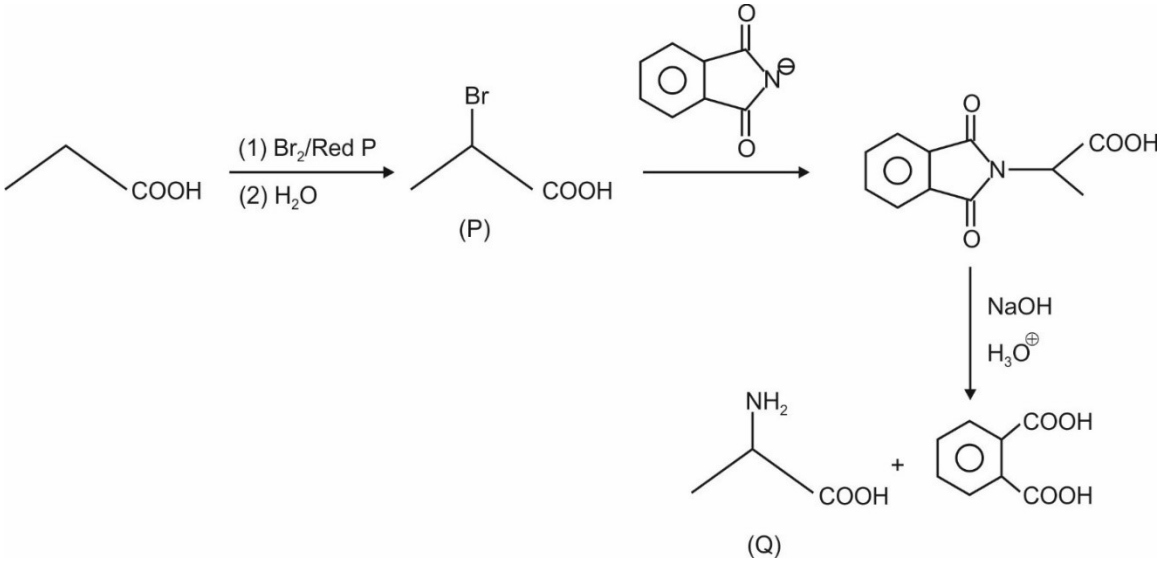
(B) Treating **P** with conc. NH_4OH solution followed by acidification gives Q.

(C) Treating **Q** with a solution of $NaNO_2$ in aq. HCl liberates N_2.

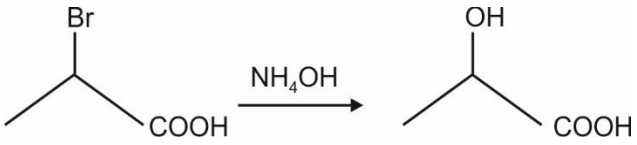
(D) **P** is more acidic than CH_3CH_2COOH.

Answer (C, D)

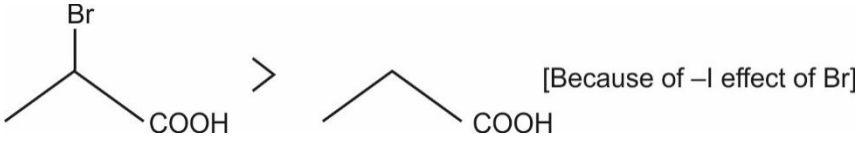
Sol.



→ $NaBH_4$ cannot reduce acids

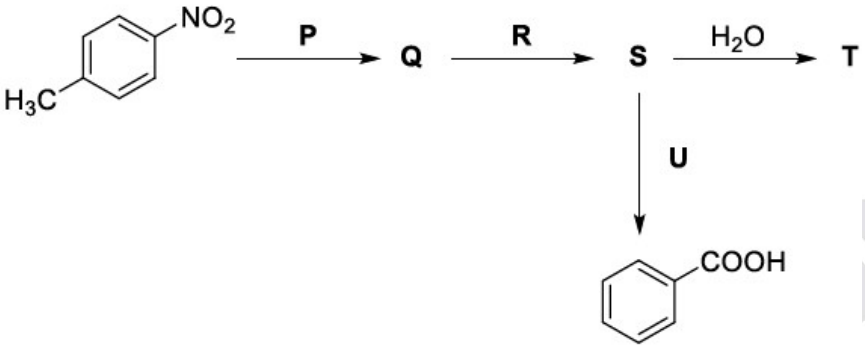
→ 

→ 1° amine on reaction with $NaNO_2/HCl$ liberates N_2 gas.

→ 

[Because of –I effect of Br]

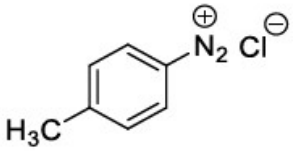
14. Considering the following reaction sequence,

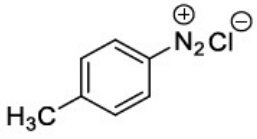


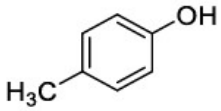
the correct option(s) is(are)

(A) **P** = H_2/Pd, ethanol **R** = $NaNO_2/HCl$ **U** = 1. H_3PO_2

2. $KMnO_4$ – KOH, heat

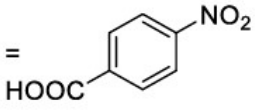
(B) **P** = Sn/HCl **R** = HNO_2 **S** = 

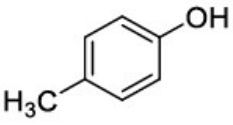
(C) **S** = 

T = 

U = 1. CH_3CH_2OH

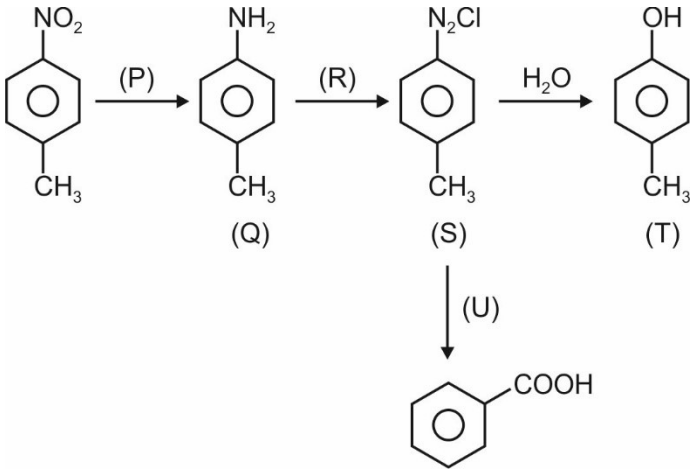
2. $KMnO_4$ – KOH, heat

(D) **Q** = 

R = H_2/Pd, ethanol **T** = 

Answer (A, B, C)

Sol.



→ P may be → H_2/Pd, ethanol; Sn/HCl

→ R may be → $NaNO_2$/HCl; HNO_2

→ U may be → (i) H_3PO_2, (ii) $KMnO_4$ – KOH, Δ or (i) $CH_3 – CH_2 – OH$, (ii) $KMnO_4$ – KOH, Δ

SECTION – 3 (Maximum marks : 12)

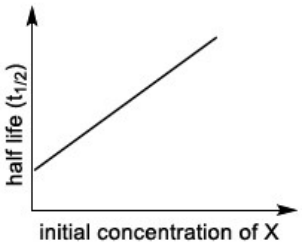
- This section contains **FOUR (04)** Matching List Sets.
- Each set has **ONE** Multiple Choice Question.
- Each set has **TWO** lists: **List-I** and **List-II**.
- **List-I** has **Four** entries (I), (II), (III) and (IV) and **List-II** has **Five** entries (P), (Q), (R), (S) and (T).
- FOUR options 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	:	+3	**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.

15. Match the rate expressions in LIST-I for the decomposition of X with the corresponding profiles provided in LIST-II. X_s and k are constants having appropriate units.

LIST-I **LIST-II**

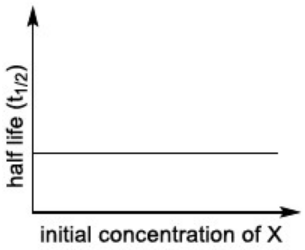
(I) $\text{rate} = \dfrac{k[X]}{X_s + [X]}$ (P)



under all possible initial concentrations of X

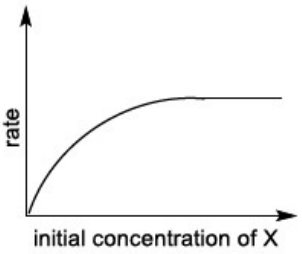
(II) $\text{rate} = \dfrac{k[X]}{X_s + [X]}$

where initial concentrations of X are much less than X_s

(Q) 

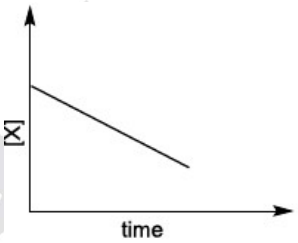
(III) $\text{rate} = \dfrac{k[X]}{X_s + [X]}$

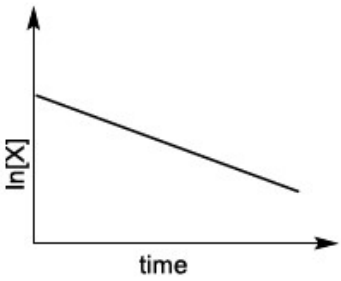
where initial concentrations of X are much higher than X_s

(R) 

(IV) $\text{rate} = \dfrac{k[X]^2}{X_s + [X]}$

where initial concentration of X is much higher than X_s

(S) 

(T) 

(A) I→ P; II→ Q; III → S; IV → T

(B) I→ R; II→ S; III → S; IV → T

(C) I→ P; II→ Q; III → Q; IV → R

(D) I→ R; II→ S; III → Q; IV → R

Answer (A)

Sol. (I) $\text{rate} = \dfrac{k[X]}{X_s + [X]}$

Case-1: $[X] >> X_s$; $[X] + X_s \approx [X]$

$\text{rate} = \dfrac{k[X]}{[X]} = k$ (Zero order w.r.t. X)

I → P, S

Case-2: $[X] << X_s$; $[X] + X_s \approx X_s$

$\therefore \quad \text{rate} = \dfrac{k[X]}{X_s} = k'[X]$ (1^{st} order w.r.t. X)

$\therefore \quad I \rightarrow Q, T$

Case-3: $[X] \approx X_s$

$$\text{rate} = \frac{k[X]}{X_s + [X]}$$

In this case curve-R given in List-II will match.

$\therefore \quad I \rightarrow P, Q, R, S, T$ (The graph of half-life should start from origin)

(II) $$\text{rate} = \frac{k[X]}{X_s + [X]}$$

$\because \quad [X] << X_s$

$\therefore \quad X_s + [X] \approx X_s$

$\therefore \quad \text{rate} = \dfrac{k[X]}{X_s} = k'[X]$ (1^{st} order w.r.t. X)

$\therefore \quad II \rightarrow Q, T$

(III) $$\text{rate} = \frac{k[X]}{X_s + [X]}$$

$\because \quad [X] >> X_s$

$\therefore \quad X_s + [X] \approx [X]$

$\therefore \quad \text{rate} = \dfrac{k[X]}{[X]} = k$ (Zero order w.r.t. X)

$\therefore \quad III \rightarrow P, S$

(IV) $$\text{rate} = \frac{k[X]^2}{X_s + [X]}$$

$\because \quad [X] >> X_s$

$\therefore \quad X_s + [X] \approx [X]$

$\therefore \quad \text{rate} = \dfrac{k[X]^2}{[X]} = k[X]$ (1^{st} order w.r.t. X)

$\therefore \quad IV \rightarrow Q, T$

16. LIST-I contains compounds and LIST-II contains reactions

LIST-I	**LIST-II**
(I) H_2O_2	(P) $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow$
(II) $Mg(OH)_2$	(Q) $BaO_2 + H_2SO_4 \rightarrow$
(III) $BaCl_2$	(R) $Ca(OH)_2 + MgCl_2 \rightarrow$
(IV) $CaCO_3$	(S) $BaO_2 + HCl \rightarrow$
	(T) $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow$

Match each compound in LIST-I with its formation reaction(s) in LIST-II, and choose the correct option

(A) I → Q; II → P; III → S; IV → R

(B) I → T; II → P; III → Q; IV → R

(C) I → T; II → R; III → Q; IV → P

(D) I → Q; II → R; III → S; IV → P

Answer (D)

Sol. (P) $Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$

(Q) $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$

(R) $Ca(OH)_2 + MgCl_2 \longrightarrow Mg(OH)_2 + CaCl_2$

(S) $BaO_2 + 2HCl \longrightarrow BaCl_2 + H_2O_2$

(T) $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$

I → Q

II → R

III → S

IV → P

Option (D) is correct.

17. LIST-I contains metal species and LIST-II contains their properties.

LIST-I	**LIST-II**
(I) $[Cr(CN)_6]^{4-}$	(P) t_{2g} orbitals contain 4 electrons
(II) $[RuCl_6]^{2-}$	(Q) μ(spin-only) = 4.9 BM
(III) $[Cr(H_2O)_6]^{2+}$	(R) low spin complex ion
(IV) $[Fe(H_2O)_6]^{2+}$	(S) metal ion in 4+ oxidation state
	(T) d^4 species

[Given: Atomic number of Cr = 24, Ru = 44, Fe = 26]

Match each metal species in LIST-I with their properties in LIST-II, and choose the correct option

(A) I → R, T; II → P, S; III → Q, T; IV → P, Q

(B) I → R, S; II → P, T; III → P, Q; IV → Q, T

(C) I → P, R; II → R, S; III → R, T; IV → P, T

(D) I → Q, T; II → S, T; III → P, T; IV → Q, R

Answer (A)

Sol. (I) $[Cr(CN)_6]^{4-}$

$Cr^{+2} = [Ar]\ 3d^4\ 4s^0$

It is d^2sp^3 hybridised as CN^- is a strong field ligand.

(II) $[RuCl_6]^{2-}$

$Ru^{+4} = [Kr]\ 4d^4\ 5s^0$

t_{2g} set contains 4 electron.

(III) $[Cr(H_2O)_6]^{2+}$

$Cr^{+2} = [Ar]\ 3d^4\ 4s^0$

It has 4 unpaired e^- as H_2O is weak field ligand.

So, its μ = 4.9 B.M.

(IV) $[Fe(H_2O)_6]^{2+}$

$Fe^{2+} = [Ar]3d^6\ 4s^0$

$= t_{2g}^4\ e_g^2$

It has 4 unpaired e^-, its μ = 4.9 B.M.

18. Match the compounds in LIST-I with the observations in LIST-II, and choose the correct option.

LIST-I	**LIST-II**
(I) Aniline	(P) Sodium fusion extract of the compound on boiling with $FeSO_4$, followed by acidification with conc. H_2SO_4, gives Prussian blue color.
(II) o-Cresol	(Q) Sodium fusion extract of the compound on treatment with sodium nitroprusside gives blood red color.
(III) Cysteine	(R) Addition of the compound to a saturated solution of $NaHCO_3$ results in effervescence.
(IV) Caprolactam	(S) The compound reacts with bromine water to give a white precipitate.
	(T) Treating the compound with neutral $FeCl_3$ solution produces violet color.

(A) I → P, Q; II → S; III → Q, R; IV → P

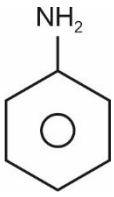
(B) I → P; II → R, S; III → R; IV → Q, S

(C) I → Q, S; II → P, T; III → P; IV → S

(D) I → P, S; II → T; III → Q, R; IV → P

Answer (D)

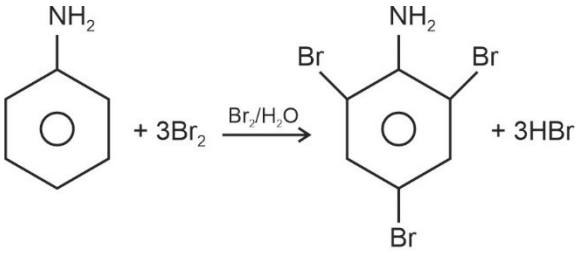
Sol. (I)



Since it contains both carbon and nitrogen so its sodium fusion extract with boiling $FeSO_4$, followed by acidification with conc. H_2SO_4 gives Prussian blue colour.

$Fe^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-}$

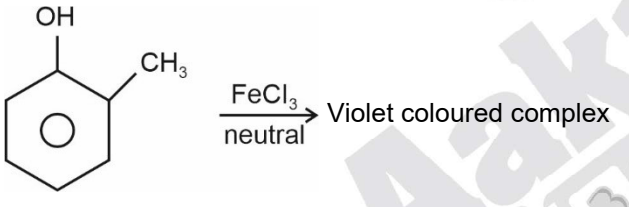
$$3[Fe(CN_6)]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3 \cdot xH_2O}$$



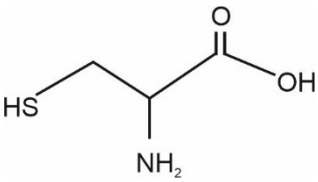
white ppt

I - (P, S)

(II) o-Cresol

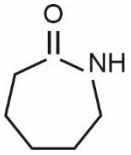


(III) Cysteine



Since it has both, sulphur and nitrogen, so its sodium fusion extract will give blood red colour with Fe^{3+} and it has carboxylic group so it will give effervescence with $NaHCO_3$.

(IV) Caprolactam



Its sodium fusion extract will give Prussian blue colour on boiling with $FeSO_4$ followed by acidification with conc. H_2SO_4.