PART-II : CHEMISTRY

SECTION - 1

- This section contains **EIGHT (08)** questions.
- Each question has **FOUR** options (A), (B), (C) & (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	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, and 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;

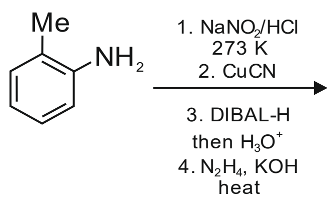
choosing ONLY (B) will get +1 mark;

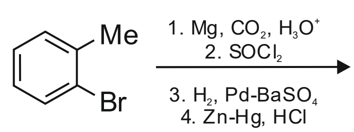
choosing ONLY (D) will get +1 mark;

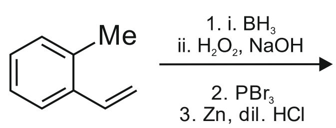
choosing no option (i.e., the question is unanswered) will get 0 marks; and

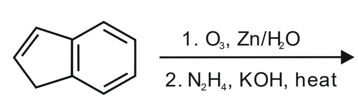
choosing any other combination of options will get –2 mark.

1. The reaction sequence(s) that would lead to *o*-xylene as the major product is(are)

(A) 

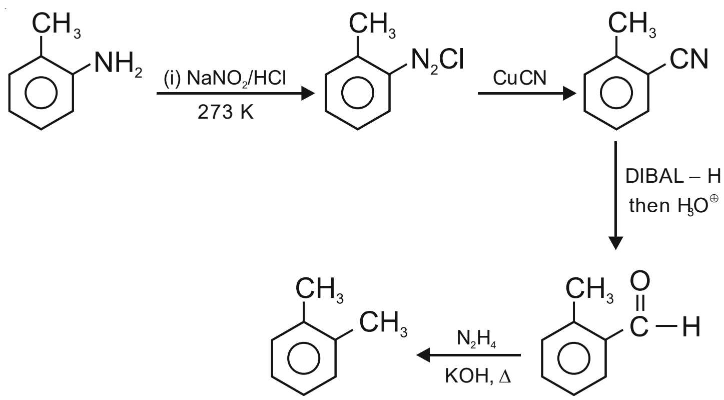
(B) 

(C) 

(D) 

Answer (A, B)

Sol. (A)



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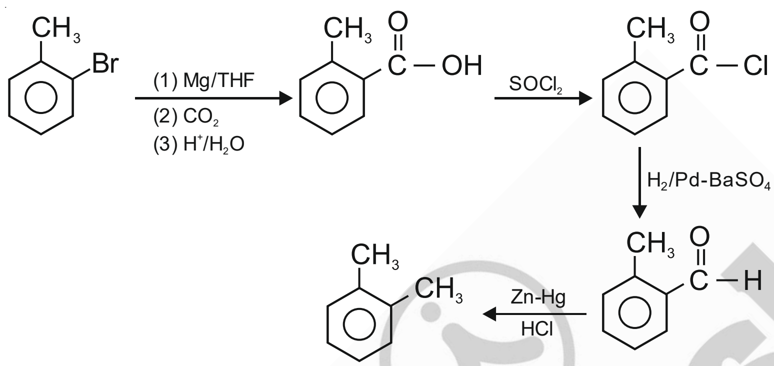
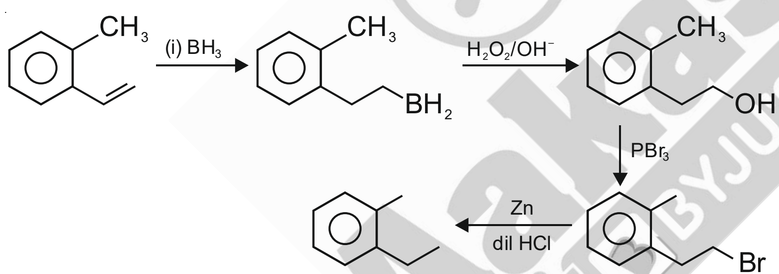
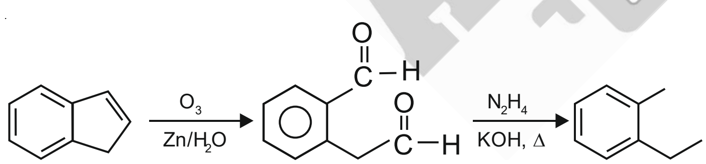


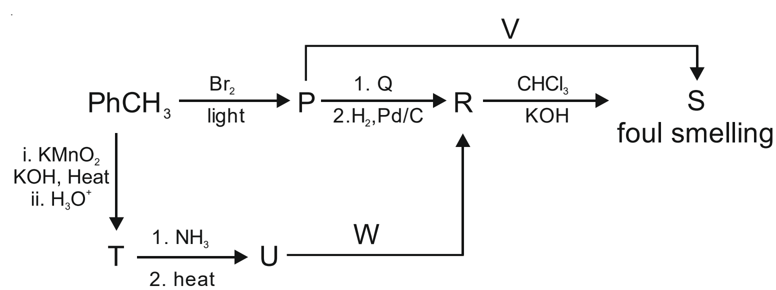
(C)



(D)



2. Correct option(s) for the following sequence of reactions is(are)



(A) Q = KNO_2, W = $LiAlH_4$

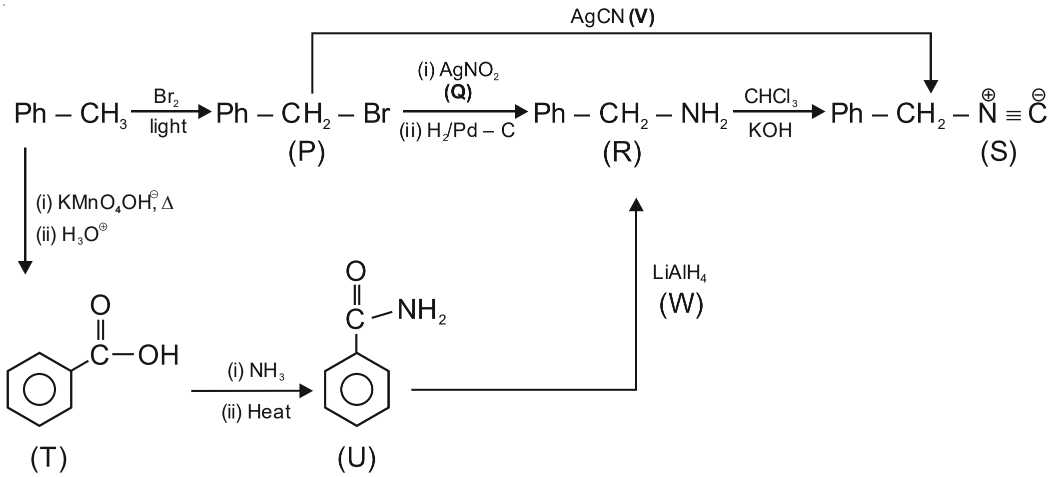
(B) R = benzenamine, V = KCN

(C) Q = $AgNO_2$, R = phenylmethanamine

(D) W = $LiAlH_4$, V = AgCN

Answer (C, D)

Sol.



∴ Correct option are

$Q = AgNO_2$, R = phenylmethanamine

$W = LiAlH_4$, V = AgCN

3. For the following reaction

$$2X + Y \xrightarrow{k} P$$

the rate of reaction is $\frac{d[P]}{dt} = k[X]$. Two moles of X are mixed with one mole of Y to make 1.0 L of solution. At 50 s, 0.5 mole of Y is left in the reaction mixture. The correct statement(s) about the reaction is(are)

(Use: ln 2 = 0.693)

(A) The rate constant, k, of the reaction is $13.86 \times 10^{-4}\ s^{-1}$.

(B) Half-life of X is 50 s.

(C) At 50 s, $-\frac{d[X]}{dt} = 13.86 \times 10^{-3}$ mol L^{-1} s^{-1}.

(D) At 100 s, $-\frac{d[Y]}{dt} = 3.46 \times 10^{-3}$ mol L^{-1} s^{-1}.

Answer (B,C,D)

Sol. rate $= \frac{d[P]}{dt} = k[X]$

2X	+	Y	→	P
2 mole		1 mole		
1 mole		0.5 mole		0.5 mole

$$-\frac{d[X]}{dt} = k_1[X] = 2k[X] \Rightarrow 2k = k_1$$

$$-\frac{d[Y]}{dt} = k_2[X] = k[X] \Rightarrow k_2 = k$$

$$2k = \frac{1}{50}\ln 2$$

$$k = \frac{1}{100}\ln 2 = \frac{0.693}{100} = 6.93 \times 10^{-3}\ s^{-1}$$

$$(t_{1/2})_x = \frac{\ln 2}{k_1} = \frac{\ln 2 \times 100}{2 \times 0.693} = 50\ sec$$

At 50 sec

$$-\frac{d[X]}{dt} = 2k[X] = 2 \times \frac{0.693}{100} \times 1$$

$$= 13.86 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$$

At 100 sec

$$-\frac{d[Y]}{dt} = k_2[X] = k[X] = \frac{0.693}{100} \times \frac{1}{2}$$

($\because$ Concentration of X after 2 half lives = $\frac{1}{2}$ M)

$$= 3.46 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}$$

4. Some standard electrode potentials at 298 K are given below:

Pb^{2+}/Pb	–0.13 V
Ni^{2+}/Ni	–0.24 V
Cd^{2+}/Cd	–0.40 V
Fe^{2+}/Fe	–0.44 V

To a solution containing 0.001 M of X^{2+} and 0.1 M of Y^{2+}, the metal rods X and Y are inserted (at 298 K) and connected by a conducting wire. This resulted in dissolution of X. The correct combination(s) of X and Y, respectively, is(are)

(Given: Gas constant, R = 8.314 J K^{-1} mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

(A) Cd and Ni
(B) Cd and Fe
(C) Ni and Pb
(D) Ni and Fe

Answer (A,B,C)

Sol. $X + Y^{2+} \rightarrow X^{2+} + Y$

$$E = E^\circ - \frac{0.06}{2}\log_{10}\left(\frac{10^{-3}}{10^{-1}}\right)$$

E = E° + 0.06

(A) E° = –(– .4) + (– .24) = .16 > 0

(B) E° = –(– .4) + (– .44) = –.04 < 0 and E_{cell} = –0.04 + 0.06 = +0.02 > 0

(C) E° = –(– .24) + (– .13) = .11 > 0

(D) E° = –(– .24) + (– .44) = –.2 < 0

$\therefore$ E_{cell} = –0.2 + 0.06 = –0.14 < 0

$\therefore$ If E_{cell} > 0 then the cell construction is possible.

5. The pair(s) of complexes wherein both exhibit tetrahedral geometry is(are)

(Note: py = pyridine

Given: Atomic numbers of Fe, Co, Ni and Cu are 26, 27, 28 and 29, respectively)

(A) $[FeCl_4]^-$ and $[Fe(CO)_4]^{2-}$

(B) $[Co(CO)_4]^-$ and $[CoCl_4]^{2-}$

(C) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$

(D) $[Cu(py)_4]^+$ and $[Cu(CN)_4]^{3-}$

Answer (A,B,D)

Sol. $[FeCl_4]^- \rightarrow Fe^{3+}, 3d^5$ (weak field ligand) = sp^3

$[Fe(CO)_4]^{-2} \rightarrow Fe^{2-}, 3d^{10} \rightarrow sp^3$

$[Co(CO)_4]^- \rightarrow Co^-, 3d^{10} \rightarrow sp^3$

$[CoCl_4]^{2-} \rightarrow Co^{2+}, 3d^7$ (weak field ligand) $\rightarrow sp^3$

$[Ni(CO)_4] \rightarrow Ni, 3d^{10} \rightarrow sp^3$

$[Ni(CN)_4]^{2-} \rightarrow Ni^{2+}, 3d^8$ (strong field ligand) $\rightarrow dsp^2$

$[Cu(py)_4]^+ \rightarrow Cu^+, 3d^{10} \rightarrow sp^3$

$[Cu(CN)_4]^{3-} \rightarrow Cu^+, 3d^{10} \rightarrow sp^3$

In $3d^{10}$ electronic configuration only sp^3 hybridisation and tetrahedral geometry is possible.

6. The correct statement(s) related to oxoacids of phosphorous is(are)

(A) Upon heating, H_3PO_3 undergoes disproportionation reaction to produce H_3PO_4 and PH_3.

(B) While H_3PO_3 can act as reducing agent, H_3PO_4 cannot.

(C) H_3PO_3 is a monobasic acid.

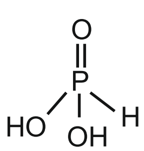
(D) The H atom of P-H bond in H_3PO_3 is not ionizable in water.

Answer (A,B,D)

Sol. $4H_3PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$

In H_3PO_4, phosphorous is present in highest oxidation state, i.e., +5. So H_3PO_4 cannot acts as reducing agent.

Structure of H_3PO_3,



It is a dibasic acid.

H atom present in P–H bond is not ionizable.

These P-H bonds are not ionisable to give H^+ and do not play any role in basicity. Only those H atoms which are attached with oxygen in P-OH form are ionisable and cause the basicity. Thus, H_3PO_3 and H_3PO_4 are dibasic and tribasic, respectively as the structure of H_3PO_3 has two P–OH bonds and H_3PO_4 three.

SECTION - 2

- This section contains **THREE (03)** question stems.
- There are TWO (02) questions corresponding to each question stem.
- The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value corresponding to the answer in the designated place using the mouse and the on-screen virtual numeric keypad.
- 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 : +2 If ONLY the correct numerical value is entered at the designated place.

Zero Marks : 0 In all other cases.

Question Stem for Question Nos. 7 and 8

Question Stem

At 298 K, the limiting molar conductivity of a weak monobasic acid is 4×10^2 S cm^2 mol^{-1}. At 298 K, for an aqueous solution of the acid the degree of dissociation is α and the molar conductivity is $y \times 10^2$ S cm^2 mol^{-1}. At 298 K, upon 20 times dilution with water, the molar conductivity of the solution becomes $3y \times 10^2$ S cm^2 mol^{-1}.

7. The value of α is _______.

Answer (0.215)

8. The value of y is _______.

Answer (0.86)

Sol. Solution of Question Nos. 7 and 8

Molar conductivity of HX at infinite dilution

$\Lambda_m^\infty = 4 \times 10^2$ S cm^2 mol^{-1}

Molar conductivity of HX at conc. $c_1 = y \times 10^2$ S cm^2 mol^{-1}

$$\alpha_1 = \frac{\Lambda_m^{c_1}}{\Lambda_m^\infty} = \frac{y \times 10^2}{4 \times 10^2} = \frac{y}{4}$$

On 20 times dilution of the solution of HX

$$\alpha_2 = \frac{\Lambda_m^{c_2}}{\Lambda_m^\infty} = \frac{3y \times 10^2}{4 \times 10^2} = \frac{3y}{4} \qquad \left[c_2 = \frac{c_1}{20}\right]$$

$$\frac{\alpha_1}{\alpha_2} = \frac{1}{3} \qquad \Rightarrow \alpha_2 = 3\alpha_1$$

$$\begin{array}{ccccc} HX & \rightleftharpoons & H^+ & + & X^- \\ c_1(1-\alpha_1) & & c_1\alpha_1 & & c_1\alpha_1 \end{array}$$

$$K_a = \frac{c_1\alpha_1^2}{1-\alpha_1} = \frac{c_2\alpha_2^2}{1-\alpha_2} = \frac{c_1(3\alpha_1)^2}{20(1-3\alpha_1)}$$

$$\frac{1}{1-\alpha_1} = \frac{9}{20(1-3\alpha_1)}$$

$20 - 60\alpha_1 = 9 - 9\alpha_1 \quad \Rightarrow \quad \alpha_1 = \frac{11}{51} = 0.215$

$y = 4\alpha_1 = 0.86$

Question Stem for Question Nos. 9 and 10

Question Stem

Reaction of x g of Sn with HCl quantitatively produced a salt. Entire amount of the salt reacted with y g of nitrobenzene in the presence of required amount of HCl to produce 1.29 g of an organic salt (quantitatively).

(Use Molar masses (in g mol^{-1}) of H, C, N, O, Cl and Sn as 1, 12, 14, 16, 35 and 119, respectively).

9. The value of x is ________.

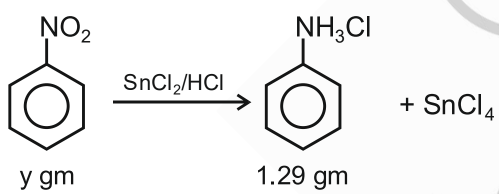
Answer (3.57)

10. The value of y is ________.

Answer (1.23)

Sol. Solution of Question Nos. 9 and 10

$Sn + HCl \rightarrow SnCl_2$



$\Rightarrow$ Moles of ammonium salt = $\frac{1.29}{129} = 0.01$

$\Rightarrow$ Moles of nitrobenzene = 0.01

$\Rightarrow$ y = 0.01 × Molar mass of nitrobenzene

= 0.01 × 123

y = 1.23

Also

No. of eq. of nitrobenzene = No. of eq. of $SnCl_2$

$6 \times (0.01) = 2 \times n_{SnCl_2}$

$n_{SnCl_2} = 0.03$

$\Rightarrow n_{Sn} = 0.03$

$w_{Sn} = 0.03 \times 119$

x = 3.57

Question Stem for Question Nos. 11 and 12

Question Stem

A sample (5.6 g) containing iron is completely dissolved in cold dilute HCl to prepare a 250 mL of solution. Titration of 25.0 mL of this solution requires 12.5 mL of 0.03 M $KMnO_4$ solution to reach the end point. Number of moles of Fe^{2+} present in 250 mL solution is x × 10^{-2} (consider complete dissolution of $FeCl_2$). The amount of iron present in the sample is y% by weight.

(Assume: $KMnO_4$ reacts only with Fe^{2+} in the solution

Use: Molar mass of iron as 56 g mol^{-1})

11. The value of x is ________.

Answer (1.875)

12. The value of y is ________.

Answer (18.75)

Sol. Solution of Question Nos. 11 and 12

$8H^+ + 5Fe^{2+} + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

For 25 ml,

meq of Fe^{2+} = meq of MnO_4^-

= 12.5 × 0.03 × 5

For 250 ml,

mmoles of $Fe^{2+} = \frac{12.5 \times 0.03 \times 5 \times 250}{25}$

moles of $Fe^{2+} = \frac{18.75}{1000}$ mol

= 18.75×10^{-3} mol

= 1.875×10^{-2} mol

x = 1.875

Weight of Fe^{2+} = $1.875 \times 10^{-2} \times 56$ = 1.05 g

% purity of $Fe^{2+} = \frac{1.05}{5.6} \times 100$ = 18.75%

y = 18.75%

SECTION - 3

- This section contains **TWO (02) paragraphs**. Based on each paragraph, there are **TWO (02)** 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.

Paragraph

The amount of energy required to break a bond is same as the amount of energy released when the same bond is formed. In gaseous state, the energy required for homolytic cleavage of a bond is called Bond Dissociation Energy (BDE) or Bond Strength. BDE is affected by *s*-character of the bond and the stability of the radicals formed. Shorter bonds are typically stronger bonds. BDEs for some bonds are given below:

$$H_3C-H(g) \longrightarrow H_3\dot{C}(g) + \dot{H}(g) \quad \Delta H^\circ = 105 \text{ kcal mol}^{-1}$$

$$Cl-Cl(g) \longrightarrow \dot{Cl}(g) + \dot{Cl}(g) \quad \Delta H^\circ = 58 \text{ kcal mol}^{-1}$$

$$H_3C-Cl(g) \longrightarrow H_3\dot{C}(g) + \dot{Cl}(g) \quad \Delta H^\circ = 85 \text{ kcal mol}^{-1}$$

$$H-Cl(g) \longrightarrow \dot{H}(g) + \dot{Cl}(g) \quad \Delta H^\circ = 103 \text{ kcal mol}^{-1}$$

13. Correct match of the **C-H** bonds (shown in bold) in Column **J** with their BDE in Column **K** is

Column J		Column K
Molecule		**BDE (kcal mol^{-1})**
(P) **H-C**H$(CH_3)_2$	(i)	132
(Q) **H-C**H_2Ph	(ii)	110
(R) **H-C**H=CH_2	(iii)	95
(S) **H-C**≡CH	(iv)	88

(A) P – iii, Q – iv, R – ii, S – i

(B) P – i, Q – ii, R – iii, S – iv

(C) P – iii, Q – ii, R – i, S – iv

(D) P – ii, Q – i, R – iv, S – iii

Answer (A)

Sol. $H-CH(CH_3)_2 \longrightarrow H\dot{C}(CH_3)-CH_3$

$H-CH_2Ph \longrightarrow {}^\bullet CH_2-Ph$
Benzyl radical

$H-CH=CH_2 \rightarrow {}^\bullet CH=CH_2$

$H-C\equiv CH \rightarrow {}^\bullet C\equiv CH$

Order of stability of free radical

Q > P > R > S

Stability of free radical $\propto \dfrac{1}{\text{Bond energy}}$

$\therefore$ Order of bond energy :

S > R > P > Q

14. For the following reaction

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{light}} CH_3Cl(g) + HCl(g)$$

the correct statement is

(A) Initiation step is exothermic with $\Delta H° = -58$ kcal mol^{-1}

(B) Propagation step involving $^{\bullet}CH_3$ formation is exothermic with $\Delta H° = -2$ kcal mol^{-1}

(C) Propagation step involving CH_3Cl formation is endothermic with $\Delta H° = +27$ kcal mol^{-1}

(D) The reaction is exothermic with $\Delta H° = -25$ kcal mol^{-1}

Answer (D)

Sol. (1) $Cl_2 \rightarrow 2Cl^{\bullet}$ (Initiation step) $\Delta H = 58$ kcal/mol

(2) $CH_4 + Cl^{\bullet} \rightarrow {}^{\bullet}CH_3 + HCl$

(3) ${}^{\bullet}CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

] Propagation step

Step (1) → Endothermic (bond breaking)

Step (2) → $\Delta H = 105 - 103$

$= 2$ kcal/mol (Endothermic)

Step (3) → $\Delta H = 58 - 85$

$= -27$ kcal/mol (Exothermic)

For complete reaction

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{light}} CH_3Cl(g) + HCl(g)$$

$\Delta H = 58 + 105 - 85 - 103$

$= -25$ kcal/mol

Paragraph

The reaction of $K_3[Fe(CN)_6]$ with freshly prepared $FeSO_4$ solution produces a dark blue precipitate called Turnbull's blue. Reaction of $K_4[Fe(CN)_6]$ with the $FeSO_4$ solution in complete absence of air produces a white precipitate X, which turns blue in air. Mixing the $FeSO_4$ solution with $NaNO_3$, followed by a slow addition of concentrated H_2SO_4 through the side of the test tube produces a brown ring.

15. Precipitate X is

(A) $Fe_4[Fe(CN)_6]_3$

(B) $Fe[Fe(CN)_6]$

(C) $K_2Fe[Fe(CN)_6]$

(D) $KFe[Fe(CN)_6]$

Answer (C)

16. Among the following, the brown ring is due to the formation of

(A) $[Fe(NO)_2(SO_4)_2]^{2-}$

(B) $[Fe(NO)_2(H_2O)_4]^{3+}$

(C) $[Fe(NO)_4(SO_4)_2]$

(D) $[Fe(NO)(H_2O)_5]^{2+}$

Answer (D)

Sol. Solution of Question Nos. 15 and 16

$$Fe^{2+} + K_3[Fe(CN)_6] \rightarrow \underset{\text{Turnbull's blue ppt.}}{Fe_3[Fe(CN)_6]_2} \downarrow$$

$$Fe^{2+} + K_4[Fe(CN)_6] \xrightarrow[\text{of air}]{\text{in absence}} \underset{\text{White ppt. (X)}}{K_2Fe[Fe(CN)_6]} \downarrow$$

In air Fe^{2+} gets oxidised to Fe^{3+}

$$Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} \downarrow$$

$$2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2NO\uparrow + 4SO_4^{2-} + 4H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\substack{\text{Compound responsible}\\ \text{for brown ring}}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

$\therefore$ X = $K_2Fe[Fe(CN)_6]$

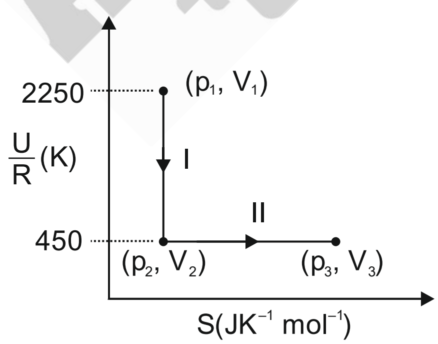
Brown ring is due to $[Fe(H_2O)_5NO]^{2+}$

SECTION - 4

- This section contains THREE (03) questions.
- The answer to each question is a NON-NEGATIVE INTEGER.
- For each question, enter the correct integer corresponding to the answer using the mouse and the on-screen 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	:	+4	If ONLY the correct integer is entered;
Zero Marks	:	0	In all other cases.

17. One mole of an ideal gas at 900 K, undergoes two reversible processes, I followed by II, as shown below. If the work done by the gas in the two processes are same, the value of $\ln\frac{V_3}{V_2}$ is ____.



(U: internal energy, S: entropy, p: pressure, V: volume, R: gas constant)

(Given: molar heat capacity at constant volume, $C_{V,m}$ of the gas is $\frac{5}{2}R$)

Answer (10)

Sol. Process I is adiabatic reversible

Process II is reversible isothermal process

Process I - (Adiabatic Reversible)

$$\frac{\Delta U}{R} = 450 - 2250$$

$\Delta U = -1800R$

$W_I = \Delta U = -1800R$

Process II - (Reversible Isothermal Process)

$T_1 = 900$ K

Calculation of T_2 after reversible adiabatic process

$-1800R = nC_v(T_2 - T_1)$

$$-1800R = 1 \times \frac{5}{2}R(T_2 - 900)$$

$T_2 = 180$ K

$$W_{II} = -nRT_2 \ln\frac{v_3}{v_2} = W_I$$

$$\Rightarrow \quad -1 \times R \times 180 \ln\frac{v_3}{v_2} = -1800R$$

$$\ln\frac{v_3}{v_2} = 10$$

18. Consider a helium (He) atom that absorbs a photon of wavelength 330 nm. The change in the velocity (in cm s^{-1}) of He atom after the photon absorption is_____.

(Assume: Momentum is conserved when photon is absorbed.

Use: Planck constant = 6.6×10^{-34} J s, Avogadro number = 6×10^{23} mol^{-1}, Molar mass of He = 4 g mol^{-1})

Answer (30)

Sol. Momentum of photon $= \frac{h}{\lambda} = \frac{6.6 \times 10^{-27}}{330 \times 10^{-7}}$ gm cm s^{-1}

Momentum of 1 mole of He-atoms = $m\Delta v$

$$\therefore \quad m\Delta v = N_A \times \frac{h}{\lambda}$$

$$4 \times \Delta v = \frac{6 \times 10^{23} \times 6.6 \times 10^{-27}}{330 \times 10^{-7}}$$

$$\Delta v = \frac{6 \times 6.6 \times 10^2}{33 \times 4} = 30 \text{ cm s}^{-1}$$

$\therefore$ Change in velocity of He-atoms = 30 cm s^{-1}

19. Ozonolysis of ClO_2 produces an oxide of chlorine. The average oxidation state of chlorine in this oxide is ____.

Answer (6)

Sol. ClO_2 contains an odd electron and is paramagnetic. It reacts with ozone to give O_2 and Cl_2O_6.

$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$

In Cl_2O_6, the average oxidation state of Cl is +6.