## 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 <br> which are correct; |
| Partial Marks | $:$ | +1 | If two or more options are correct but ONLY one option is chosen and it is a correct <br> 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)




(B)




(C)



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

(A) $\mathrm{Q}=\mathrm{KNO}_{2}, \mathrm{~W}=\mathrm{LiAlH}_{4}$
(B) $\mathrm{R}=$ benzenamine, $\mathrm{V}=\mathrm{KCN}$
(C) $\mathrm{Q}=\mathrm{AgNO}_{2}, \mathrm{R}=$ phenylmethanamine
(D) $\mathrm{W}=\mathrm{LiAlH}_{4}, \mathrm{~V}=\mathrm{AgCN}$

Answer (C, D)
$\operatorname{AgCN}(\mathrm{V})$

Sol.


$\therefore \quad$ Correct option are

$$
\begin{aligned}
& \mathrm{Q}=\mathrm{AgNO}_{2}, \mathrm{R}=\text { phenylmethanamine } \\
& \mathrm{W}=\mathrm{LiAlH}_{4}, \mathrm{~V}=\mathrm{AgCN}
\end{aligned}
$$

3. For the following reaction
$2 \mathrm{X}+\mathrm{Y} \xrightarrow{\mathrm{k}} P$
the rate of reaction is $\frac{d[P]}{d t}=k[X]$. Two moles of $X$ are mixed with one mole of $Y$ to make 1.0 L of solution. At $50 \mathrm{~s}, 0.5$ 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 $13.86 \times 10^{-4} \mathrm{~s}^{-1}$.
(B) Half-life of X is 50 s .
(C) At $50 \mathrm{~s},-\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{dt}}=13.86 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$.
(D) At $100 \mathrm{~s},-\frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{dt}}=3.46 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}$.

Answer (B,C,D)
Sol. $\quad$ rate $=\frac{d[P]}{d t}=k[X]$

$$
\begin{aligned}
& 2 \mathrm{X}+\mathrm{Y} \rightarrow \mathrm{P} \\
& 2 \text { mole } 1 \text { mole } \\
& 1 \text { mole } 0.5 \text { mole } 0.5 \text { mole } \\
& -\frac{d[X]}{d t}=k_{1}[X]=2 k[X] \Rightarrow 2 k=k_{1} \\
& -\frac{\mathrm{d}[\mathrm{Y}]}{\mathrm{dt}}=\mathrm{k}_{2}[\mathrm{X}]=\mathrm{k}[\mathrm{X}] \Rightarrow \mathrm{k}_{2}=\mathrm{k} \\
& 2 \mathrm{k}=\frac{1}{50} \ln 2
\end{aligned}
$$

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

$$
\left(\mathrm{t}_{1 / 2}\right)_{\mathrm{x}}=\frac{\ln 2}{\mathrm{k}_{1}}=\frac{\ln 2 \times 100}{2 \times 0.693}=50 \mathrm{sec}
$$

At 50 sec

$$
\begin{aligned}
-\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{dt}}=2 \mathrm{k}[\mathrm{X}] & =2 \times \frac{0.693}{100} \times 1 \\
& =13.86 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{~s}^{-1}
\end{aligned}
$$

At 100 sec

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

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

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

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

| $\mathrm{Pb}^{2+} / \mathrm{Pb}$ | -0.13 V |
| :--- | :--- |
| $\mathrm{Ni}^{2+} / \mathrm{Ni}$ | -0.24 V |
| $\mathrm{Cd}^{2+} / \mathrm{Cd}$ | -0.40 V |
| $\mathrm{Fe}^{2+} / \mathrm{Fe}$ | -0.44 V |

To a solution containing 0.001 M of $\mathrm{X}^{2+}$ and 0.1 M of $\mathrm{Y}^{2+}$, 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, $\mathrm{R}=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$, Faraday constant, $\mathrm{F}=96500 \mathrm{C} \mathrm{mol}^{-1}$ )
(A) Cd and Ni
(B) Cd and Fe
(C) Ni and Pb
(D) Ni and Fe

Answer (A,B,C)
Sol. $X+Y^{2+} \rightarrow X^{2+}+Y$
$E=E^{\circ}-\frac{0.06}{2} \log _{10}\left(\frac{10^{-3}}{10^{-1}}\right)$
$E=E^{\circ}+0.06$
(A) $\mathrm{E}^{\circ}=-(-.4)+(-.24)=.16>0$
(B) $\mathrm{E}^{\circ}=-(-.4)+(-.44)=-.04<0$ and $\mathrm{E}_{\text {cell }}=-0.04+0.06=+0.02>0$
(C) $\mathrm{E}^{\circ}=-(-.24)+(-.13)=.11>0$
(D) $\mathrm{E}^{\circ}=-(-.24)+(-.44)=-.2<0$
$\therefore \quad \mathrm{E}_{\text {cell }}=-0.2+0.06=-0.14<0$
$\therefore$ If $\mathrm{E}_{\text {cell }}>0$ then the cell construction is possible.

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5. The pair(s) of complexes wherein both exhibit tetrahedral geometry is(are)
(Note: py = pyridine
Given: Atomic numbers of $\mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}$ and Cu are 26, 27,28 and 29 , respectively)
(A) $\left[\mathrm{FeCl}_{4}\right]^{-}$and $\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]^{2-}$
(B) $\left[\mathrm{Co}(\mathrm{CO})_{4}\right]^{-}$and $\left[\mathrm{CoCl}_{4}\right]^{2-}$
(C) $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$ and $\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$
(D) $\left[\mathrm{Cu}(\mathrm{py})_{4}\right]^{+}$and $\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]^{3-}$

Answer (A,B,D)
Sol. $\left[\mathrm{FeCl}_{4}\right]^{-} \rightarrow \mathrm{Fe}^{3+}, 3 d^{5}($ weak field ligand $)=s p^{3}$
$\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]^{-2} \rightarrow \mathrm{Fe}^{2-}, 3 d^{10} \rightarrow s p^{3}$
$\left[\mathrm{Co}(\mathrm{CO})_{4}\right]^{-} \rightarrow \mathrm{Co}^{-}, 3 d^{10} \rightarrow s p^{3}$
$\left[\mathrm{CoCl}_{4}\right]^{2-} \rightarrow \mathrm{Co}^{2+}, 3 d^{7}$ (weak field ligand) $\rightarrow s p^{3}$
$\left[\mathrm{Ni}(\mathrm{CO})_{4}\right] \rightarrow \mathrm{Ni}, 3 d^{10} \rightarrow s p^{3}$
$\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-} \rightarrow \mathrm{Ni}^{2+}, 3 d^{8}$ (strong field ligand) $\rightarrow d s p^{2}$
$\left[\mathrm{Cu}(\mathrm{py})_{4}\right]^{+} \rightarrow \mathrm{Cu}^{+}, 3 d^{10} \rightarrow s p^{3}$
$\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]^{3-} \rightarrow \mathrm{Cu}^{+}, 3 d^{10} \rightarrow s p^{3}$
In $3 d^{10}$ electronic configuration only $s p^{3}$ hybridisation and tetrahedral geometry is possible.
6. The correct statement(s) related to oxoacids of phosphorous is(are)
(A) Upon heating, $\mathrm{H}_{3} \mathrm{PO}_{3}$ undergoes disproportionation reaction to produce $\mathrm{H}_{3} \mathrm{PO}_{4}$ and $\mathrm{PH}_{3}$.
(B) While $\mathrm{H}_{3} \mathrm{PO}_{3}$ can act as reducing agent, $\mathrm{H}_{3} \mathrm{PO}_{4}$ cannot.
(C) $\mathrm{H}_{3} \mathrm{PO}_{3}$ is a monobasic acid.
(D) The H atom of $\mathrm{P}-\mathrm{H}$ bond in $\mathrm{H}_{3} \mathrm{PO}_{3}$ is not ionizable in water.

Answer (A,B,D)
Sol. $4 \mathrm{H}_{3} \mathrm{PO}_{3} \xrightarrow{\Delta} \mathrm{PH}_{3}+3 \mathrm{H}_{3} \mathrm{PO}_{4}$
In $\mathrm{H}_{3} \mathrm{PO}_{4}$, phosphorous is present in highest oxidation state, i.e., +5 . So $\mathrm{H}_{3} \mathrm{PO}_{4}$ cannot acts as reducing agent. Structure of $\mathrm{H}_{3} \mathrm{PO}_{3}$,


It is a dibasic acid.
H atom present in $\mathrm{P}-\mathrm{H}$ bond is not ionizable.
These $\mathrm{P}-\mathrm{H}$ bonds are not ionisable to give $\mathrm{H}^{+}$and do not play any role in basicity. Only those H atoms which are attached with oxygen in $\mathrm{P}-\mathrm{OH}$ form are ionisable and cause the basicity. Thus, $\mathrm{H}_{3} \mathrm{PO}_{3}$ and $\mathrm{H}_{3} \mathrm{PO}_{4}$ are dibasic and tribasic, respectively as the structure of $\mathrm{H}_{3} \mathrm{PO}_{3}$ has two $\mathrm{P}-\mathrm{OH}$ bonds and $\mathrm{H}_{3} \mathrm{PO}_{4}$ 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 : $0 \quad$ 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 $4 \times 10^{2} \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$. At 298 K , for an aqueous solution of the acid the degree of dissociation is $\alpha$ and the molar conductivity is $y \times 10^{2} \mathrm{~S} \mathrm{~cm}^{2}$ $\mathrm{mol}^{-1}$. At 298 K , upon 20 times dilution with water, the molar conductivity of the solution becomes $3 \mathrm{y} \times 10^{2} \mathrm{~S}$ $\mathrm{cm}^{2} \mathrm{~mol}^{-1}$.
7. The value of $\alpha$ is $\qquad$ .

Answer (0.215)
8. The value of $y$ is $\qquad$ .

Answer (0.86)

## Sol. Solution of Question Nos. 7 and 8

Molar conductivity of HX at infinite dilution
$\Lambda_{\mathrm{m}}^{\infty}=4 \times 10^{2} \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
Molar conductivity of HX at conc. $\mathrm{c}_{1}=\mathrm{y} \times 10^{2} \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
$\alpha_{1}=\frac{\Lambda_{\mathrm{m}}^{\mathrm{C}_{1}}}{\Lambda_{\mathrm{m}}^{\infty}}=\frac{\mathrm{y} \times 10^{2}}{4 \times 10^{2}}=\frac{\mathrm{y}}{4}$
On 20 times dilution of the solution of HX
$\alpha_{2}=\frac{\Lambda_{\mathrm{m}}^{\mathrm{c}_{2}}}{\Lambda_{\mathrm{m}}^{\infty}}=\frac{3 \mathrm{y} \times 10^{2}}{4 \times 10^{2}}=\frac{3 \mathrm{y}}{4} \quad\left[\mathrm{c}_{2}=\frac{\mathrm{c}_{1}}{20}\right]$
$\frac{\alpha_{1}}{\alpha_{2}}=\frac{1}{3} \quad \Rightarrow \alpha_{2}=3 \alpha_{1}$

$$
\left.\begin{array}{c}
\mathrm{HX} \rightleftharpoons \mathrm{H}^{+}+\mathrm{X}^{-} \\
\mathrm{c}_{1}\left(1-\alpha_{1}\right) \\
\mathrm{c}_{1} \alpha_{1} \quad \mathrm{c}_{1} \alpha_{1}
\end{array}\right] \begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{\mathrm{c}_{1} \alpha_{1}^{2}}{1-\alpha_{1}}=\frac{\mathrm{c}_{2} \alpha_{2}^{2}}{1-\alpha_{2}}=\frac{\mathrm{c}_{1}\left(3 \alpha_{1}\right)^{2}}{20\left(1-3 \alpha_{1}\right)}
\end{aligned}
$$

$$
\begin{aligned}
& \frac{1}{1-\alpha_{1}}=\frac{9}{20\left(1-3 \alpha_{1}\right)} \\
& 20-60 \alpha_{1}=9-9 \alpha_{1} \quad \Rightarrow \alpha_{1}=\frac{11}{51}=0.215 \\
& y=4 \alpha_{1}=0.86
\end{aligned}
$$

## 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 $\mathrm{g} \mathrm{mol}^{-1}$ ) of $\mathrm{H}, \mathrm{C}, \mathrm{N}, \mathrm{O}, \mathrm{Cl}$ and Sn as $1,12,14,16,35$ and 119 , respectively).
9. The value of $x$ is $\qquad$ -.

Answer (3.57)
10. The value of $y$ is $\qquad$ .

Answer (1.23)
Sol. Solution of Question Nos. 9 and 10

$$
\mathrm{Sn}+\mathrm{HCl} \rightarrow \mathrm{SnCl}_{2}
$$


$\Rightarrow$ Moles of ammonium salt $=\frac{1.29}{129}=0.01$
$\Rightarrow$ Moles of nitrobenzene $=0.01$
$\Rightarrow \mathrm{y}=0.01 \times$ Molar mass of nitrobenzene

$$
=0.01 \times 123
$$

$$
y=1.23
$$

Also
No. of eq. of nitrobenzene $=$ No. of eq. of $\mathrm{SnCl}_{2}$

$$
\begin{aligned}
6 \times(0.01) & =2 \times \mathrm{n}_{\mathrm{SnCl}_{2}} \\
\mathrm{n}_{\mathrm{SnCl}_{2}} & =0.03 \\
\Rightarrow \mathrm{n}_{\mathrm{Sn}} & =0.03 \\
\mathrm{w}_{\mathrm{Sn}} & =0.03 \times 119 \\
x & =3.57
\end{aligned}
$$

## 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 $0.03 \mathrm{M} \mathrm{KMnO}_{4}$ solution to reach the end point. Number of moles of $\mathrm{Fe}^{2+}$ present in 250 mL solution is $\mathrm{x} \times 10^{-2}$ (consider complete dissolution of $\mathrm{FeCl}_{2}$ ). The amount of iron present in the sample is $y \%$ by weight.
(Assume: $\mathrm{KMnO}_{4}$ reacts only with $\mathrm{Fe}^{2+}$ in the solution
Use: Molar mass of iron as $56 \mathrm{~g} \mathrm{~mol}^{-1}$ )
11. The value of $x$ is $\qquad$ .

Answer (1.875)
12. The value of $y$ is $\qquad$ .

Answer (18.75)
Sol. Solution of Question Nos. 11 and 12
$8 \mathrm{H}^{+}+5 \mathrm{Fe}^{2+}+\mathrm{MnO}_{4}^{-} \rightarrow 5 \mathrm{Fe}^{3+}+\mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}$
For 25 ml ,

$$
\begin{aligned}
\text { meq of } \mathrm{Fe}^{2+} & =\text { meq of } \mathrm{MnO}_{4}^{-} \\
& =12.5 \times 0.03 \times 5
\end{aligned}
$$

For 250 ml ,
mmoles of $\mathrm{Fe}^{2+}=\frac{12.5 \times 0.03 \times 5 \times 250}{25}$
moles of $\mathrm{Fe}^{2+}=\frac{18.75}{1000} \mathrm{~mol}$

$$
=18.75 \times 10^{-3} \mathrm{~mol}
$$

$$
=1.875 \times 10^{-2} \mathrm{~mol}
$$

$x=1.875$
Weight of $\mathrm{Fe}^{2+}=1.875 \times 10^{-2} \times 56=1.05 \mathrm{~g}$
$\%$ purity of $\mathrm{Fe}^{2+}=\frac{1.05}{5.6} \times 100=18.75 \%$
$y=18.75 \%$

## 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:

$\mathrm{Cl}-\mathrm{Cl}(\mathrm{g}) \longrightarrow \mathrm{Cl}(\mathrm{g})+\mathrm{Cl}(\mathrm{g}) \Delta \mathrm{H}^{\circ}=58 \mathrm{kcal} \mathrm{mol}^{-1}$
$\mathrm{H}_{3} \mathrm{C}-\mathrm{Cl}(\mathrm{g}) \longrightarrow \mathrm{H}_{3} \mathrm{C}^{\circ}(\mathrm{g})+\mathrm{Cl}(\mathrm{g}) \Delta \mathrm{H}^{\circ}=85 \mathrm{kcal} \mathrm{mol}^{-1}$
$\left.\mathrm{H}-\mathrm{Cl}(\mathrm{g}) \longrightarrow \mathrm{H}^{(\mathrm{g}} \mathrm{g}\right)+\mathrm{Cl}^{\circ}(\mathrm{g}) \Delta \mathrm{H}^{\circ}=103 \mathrm{kcal} \mathrm{mol}^{-1}$
13. Correct match of the $\mathbf{C}-\mathbf{H}$ bonds (shown in bold) in Column $\mathbf{J}$ with their BDE in Column $\mathbf{K}$ is

## Column J Column K

Molecule $\quad$ BDE ( $\mathrm{kcal} \mathrm{mol}^{-1}$ )
(P) $\mathrm{H}-\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$
(i) 132
(Q) $\mathrm{H}-\mathrm{CH}_{2} \mathrm{Ph}$
(ii) 110
(R) $\mathrm{H}-\mathrm{CH}=\mathrm{CH}_{2}$
(iii) 95
(S) $\mathrm{H}-\mathrm{C} \equiv \mathrm{CH}$
(iv) 88
(A) $P$ - iii, $Q$ - iv, $R-i i, S-i$
(B) $P$ - i, $Q$ - ii, $R$ - iii, $S$ - iv
(C) P - iii, Q - ii, $\mathrm{R}-\mathrm{i}, \mathrm{S}-\mathrm{iv}$
(D) P - ii, $\mathrm{Q}-\mathrm{i}, \mathrm{R}$ - iv, S - iii

Answer (A)
Sol.


Order of stability of free radical
$Q>P>R>S$
Stability of free radical $\propto \frac{1}{\text { Bond energy }}$
$\therefore \quad$ Order of bond energy :

$$
S>R>P>Q
$$

14. For the following reaction

$$
\mathrm{CH}_{4}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \xrightarrow{\text { light }} \mathrm{CH}_{3} \mathrm{Cl}(\mathrm{~g})+\mathrm{HCl}(\mathrm{~g})
$$

the correct statement is
(A) Initiation step is exothermic with $\Delta \mathrm{H}^{\circ}=-58 \mathrm{kcal} \mathrm{mol}^{-1}$
(B) Propagation step involving ${ }^{\bullet} \mathrm{CH}_{3}$ formation is exothermic with $\Delta \mathrm{H}^{\circ}=-2 \mathrm{kcal} \mathrm{mol}^{-1}$
(C) Propagation step involving $\mathrm{CH}_{3} \mathrm{Cl}$ formation is endothermic with $\Delta \mathrm{H}^{\circ}=+27 \mathrm{kcal} \mathrm{mol}^{-1}$
(D) The reaction is exothermic with $\Delta \mathrm{H}^{\circ}=-25 \mathrm{kcal} \mathrm{mol}^{-1}$

Answer (D)
Sol. (1) $\mathrm{Cl}_{2} \rightarrow 2 \mathrm{Cl}^{\bullet}$ (Initiation step) $\Delta \mathrm{H}=58 \mathrm{kcal} / \mathrm{mol}$
$\left.\begin{array}{l}\text { (2) } \mathrm{CH}_{4}+\mathrm{Cl} \rightarrow{ }^{\bullet} \mathrm{CH}_{3}+\mathrm{HCl} \\ \text { (3) }{ }^{\cdot} \mathrm{CH}_{3}+\mathrm{Cl}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{Cl}+\mathrm{Cl} \cdot\end{array}\right]$ Propagation step
Step (1) $\rightarrow$ Endothermic (bond breaking)
Step (2) $\rightarrow \Delta H=105-103$

$$
=2 \mathrm{kcal} / \mathrm{mol} \text { (Endothermic) }
$$

Step (3) $\rightarrow \Delta H=58-85$

$$
=-27 \mathrm{kcal} / \mathrm{mol} \text { (Exothermic) }
$$

For complete reaction

$$
\begin{aligned}
& \mathrm{CH}_{4}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \xrightarrow{\text { light }} \mathrm{CH}_{3} \mathrm{Cl}(\mathrm{~g})+\mathrm{HCl}(\mathrm{~g}) \\
& \begin{aligned}
\Delta \mathrm{H} & =58+105-85-103 \\
& =-25 \mathrm{kcal} / \mathrm{mol}
\end{aligned}
\end{aligned}
$$

## Paragraph

The reaction of $\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ with freshly prepared $\mathrm{FeSO}_{4}$ solution produces a dark blue precipitate called Turnbull's blue. Reaction of $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ with the $\mathrm{FeSO}_{4}$ solution in complete absence of air produces a white precipitate X , which turns blue in air. Mixing the $\mathrm{FeSO}_{4}$ solution with $\mathrm{NaNO}_{3}$, followed by a slow addition of concentrated $\mathrm{H}_{2} \mathrm{SO}_{4}$ through the side of the test tube produces a brown ring.
15. Precipitate X is
(A) $\mathrm{Fe}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}$
(B) $\mathrm{Fe}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
(C) $\mathrm{K}_{2} \mathrm{Fe}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
(D) $\mathrm{KFe}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$

Answer (C)
16. Among the following, the brown ring is due to the formation of
(A) $\left[\mathrm{Fe}(\mathrm{NO})_{2}\left(\mathrm{SO}_{4}\right)_{2}\right]^{2-}$
(B) $\left[\mathrm{Fe}(\mathrm{NO})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}\right]^{3+}$
(C) $\left[\mathrm{Fe}(\mathrm{NO})_{4}\left(\mathrm{SO}_{4}\right)_{2}\right]$
(D) $\left[\mathrm{Fe}(\mathrm{NO})\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{2+}$

Answer (D)

## JEE (ADVANCED)-2021 (Paper-2)

Sol. Solution of Question Nos. 15 and 16
$\mathrm{Fe}^{2+}+\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right] \rightarrow \underset{\text { Turnbull's blue ppt. }}{\mathrm{Fe}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{2} \downarrow}$
$\mathrm{Fe}^{2+}+\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right] \xrightarrow[\text { of air }]{\text { in absence }} \underset{\text { White ppt. (X) }}{\mathrm{K}_{2} \mathrm{Fe}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right] \downarrow}$
In air $\mathrm{Fe}^{2+}$ gets oxidised to $\mathrm{Fe}^{3+}$

$$
\begin{aligned}
& \mathrm{Fe}^{3+}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-} \longrightarrow \underset{\text { Prussian blue }}{\mathrm{Fe}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3} \downarrow} \\
& 2 \mathrm{NO}_{3}^{-}+4 \mathrm{H}_{2} \mathrm{SO}_{4}+6 \mathrm{Fe}^{2+} \rightarrow 6 \mathrm{Fe}^{3+}+2 \mathrm{NO} \uparrow+4 \mathrm{SO}_{4}{ }^{2-}+4 \mathrm{H}_{2} \mathrm{O} \\
& {\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}+\mathrm{NO} \longrightarrow \underset{\substack{\text { Compound responsible } \\
\text { for brown ring }}}{\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{NO}\right]^{2+}}+\mathrm{H}_{2} \mathrm{O}} \\
& \therefore \quad \mathrm{X}=\mathrm{K}_{2} \mathrm{Fe}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]
\end{aligned}
$$

Brown ring is due to $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{NO}\right]^{2+}$

## 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 : $0 \quad$ 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 $\qquad$ .

(U: internal energy, S: entropy, p: pressure, V: volume, R: gas constant)
(Given: molar heat capacity at constant volume, $\mathrm{C}_{\mathrm{V}, \mathrm{m}}$ of the gas is $\frac{5}{2} \mathrm{R}$ )
Answer (10)
Sol. Process I is adiabatic reversible
Process II is reversible isothermal process

## Process I-(Adiabatic Reversible)

$\frac{\Delta U}{R}=450-2250$
$\Delta U=-1800 R$
$\mathrm{W}_{1}=\Delta \mathrm{U}=-1800 \mathrm{R}$

## Process II - (Reversible Isothermal Process)

$\mathrm{T}_{1}=900 \mathrm{~K}$
Calculation of $T_{2}$ after reversible adiabatic process
$-1800 \mathrm{R}=\mathrm{nC} \mathrm{v}_{\mathrm{v}}\left(\mathrm{T}_{2}-\mathrm{T}_{1}\right)$
$-1800 R=1 \times \frac{5}{2} R\left(T_{2}-900\right)$
$\mathrm{T}_{2}=180 \mathrm{~K}$
$\mathrm{W}_{11}=-\mathrm{nRT}_{2} \ln \frac{\mathrm{~V}_{3}}{\mathrm{v}_{2}}=\mathrm{W}_{\mathrm{I}}$
$\Rightarrow \quad-1 \times R \times 180 \ln \frac{v_{3}}{v_{2}}=-1800 R$
$\ln \frac{v_{3}}{v_{2}}=10$
18. Consider a helium (He) atom that absorbs a photon of wavelength 330 nm . The change in the velocity (in cm $\mathrm{s}^{-1}$ ) of He atom after the photon absorption is $\qquad$ _.
(Assume: Momentum is conserved when photon is absorbed.
Use: Planck constant $=6.6 \times 10^{-34} \mathrm{~J} \mathrm{~s}$, Avogadro number $=6 \times 10^{23} \mathrm{~mol}^{-1}$, Molar mass of $\mathrm{He}=4 \mathrm{~g} \mathrm{~mol}^{-1}$ )
Answer (30)
Sol. Momentum of photon $=\frac{h}{\lambda}=\frac{6.6 \times 10^{-27}}{330 \times 10^{-7}} \mathrm{gm} \mathrm{cm} \mathrm{s}^{-1}$
Momentum of 1 mole of He -atoms $=\mathrm{m} \Delta v$
$\therefore \quad \mathrm{m} \Delta \mathrm{v}=\mathrm{N}_{\mathrm{A}} \times \frac{\mathrm{h}}{\lambda}$
$4 \times \Delta v=\frac{6 \times 10^{23} \times 6.6 \times 10^{-27}}{330 \times 10^{-7}}$
$\Delta v=\frac{6 \times 6.6 \times 10^{2}}{33 \times 4}=30 \mathrm{~cm} \mathrm{~s}^{-1}$
$\therefore \quad$ Change in velocity of He -atoms $=30 \mathrm{~cm} \mathrm{~s}^{-1}$
19. Ozonolysis of $\mathrm{ClO}_{2}$ produces an oxide of chlorine. The average oxidation state of chlorine in this oxide is $\qquad$ .
Answer (6)
Sol. $\mathrm{ClO}_{2}$ contains an odd electron and is paramagnetic. It reacts with ozone to give $\mathrm{O}_{2}$ and $\mathrm{Cl}_{2} \mathrm{O}_{6}$.
$2 \mathrm{ClO}_{2}+2 \mathrm{O}_{3} \rightarrow \mathrm{Cl}_{2} \mathrm{O}_{6}+2 \mathrm{O}_{2}$
In $\mathrm{Cl}_{2} \mathrm{O}_{6}$, the average oxidation state of Cl is +6 .

