## FINAL JEE(Advanced) EXAMINATION - 2021 <br> (Held On Sunday 03rd ${ }^{\text {rd }}$ OCTOBER, 2021) <br> PAPER-2

## PART-2 : CHEMISTRY

SECTION-1 : (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 $\quad:+4$ If only (all) the correct option(s) is(are) chosen;
Partial Marks $\quad:+3$ 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 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(s) (i.e. the question is unanswered) will get 0 marks and choosing any other option(s) will get -2 marks.

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

(B)


2. $\mathrm{N}_{2} \mathrm{H}_{4}, \mathrm{KOH}$
heat
(C)


3. Zn , dil. HCl
(D)


Ans. (A,B)

Sol.
(A)


o-Xylene
(B)


(C)


is not formed
(D)


o-Xylene is not formed
2. Correct option(s) for the following sequence of reactions is(are)

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

Ans. (C,D)

$$
\mathbf{V}(\mathrm{AgCN})
$$

Sol.


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

Ans. (B,C,D)
Sol. $\quad \frac{\mathrm{dp}}{\mathrm{dt}}=\mathrm{k}[\mathrm{x}]^{1}$

$$
\begin{array}{lll} 
& 2 \mathrm{x}+\mathrm{y} & \rightarrow \\
\mathrm{t}=0 & 2 & \mathrm{p} \\
\mathrm{t}=50 \mathrm{~s} & (2-1) \quad(1-0.5) \quad 0.5 \\
& -\frac{1}{2} \frac{\mathrm{dx}}{\mathrm{dt}}=\frac{\mathrm{dp}}{\mathrm{dt}}=\mathrm{k}[\mathrm{x}]^{1} \\
& -\frac{\mathrm{dx}}{\mathrm{dt}}=2 \mathrm{k}[\mathrm{x}]^{1} \\
& 2 \mathrm{k}=\frac{\ln 2}{50} \Rightarrow \mathrm{k}=\frac{\ln 2}{100}
\end{array}
$$

At $\quad 50 \sec \frac{-\mathrm{dx}}{\mathrm{dt}}=2 \mathrm{k} \times(1)^{1}=\frac{\ln 2}{50}$
At $\quad 100 \sec -\frac{1}{2} \frac{\mathrm{dx}}{\mathrm{dt}}=\frac{-\mathrm{dy}}{\mathrm{dt}} \Rightarrow-\frac{\mathrm{dy}}{\mathrm{dt}}=\frac{\ln 2}{100} \times \frac{1}{2}\left\{\frac{-\mathrm{dy}}{\mathrm{dt}}=\mathrm{k}[\mathrm{x}]^{1}\right\}$
4. Some standard electrode potentials at 298 K are given below:

$$
\begin{array}{ll}
\mathrm{Pb}^{2+} / \mathrm{Pb} & -0.13 \mathrm{~V} \\
\mathrm{Ni}^{2+} / \mathrm{Ni} & -0.24 \mathrm{~V} \\
\mathrm{Cd}^{2+} / \mathrm{Cd} & -0.40 \mathrm{~V} \\
\mathrm{Fe}^{2+} / \mathrm{Fe} & -0.44 \mathrm{~V}
\end{array}
$$

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

Ans. (A,B,C)
Sol. $\mathrm{x}(\mathrm{s}) \longrightarrow \mathrm{x}^{+2}(0.001 \mathrm{M})+2 \mathrm{e}^{-}$(anode)
$\mathrm{y}^{+2}(0.1 \mathrm{M})+2 \mathrm{e}^{-} \longrightarrow \mathrm{y}(\mathrm{s})$ (cathode)
$\qquad$
$\mathrm{E}_{\text {cell }}=\mathrm{E}^{\circ}{ }_{\text {cell }}-\frac{0.06}{2} \log \frac{\mathrm{x}^{+2}}{\mathrm{y}^{+2}}$
$\mathrm{E}_{\text {cell }}=\mathrm{E}^{\circ}{ }_{\text {cell }}+0.06$
(A) Cd and $\mathrm{Ni}^{\circ}{ }_{\text {cell }}=+0.4-0.24 ; \mathrm{E}_{\text {cell }}=0.22$
(B) Cd and $\mathrm{Fe} \mathrm{E}^{\circ}{ }_{\text {cell }}=-0.04 ; \mathrm{E}_{\text {cell }}=0.02$
(C) Ni and $\mathrm{Pb} \mathrm{E}^{\circ}{ }_{\text {cell }}=0.11 ; \mathrm{E}_{\text {cell }}=0.17$
(D) Ni and $\mathrm{Fe}^{\circ}{ }^{\circ}{ }_{\text {cell }}=-0.2 ; \mathrm{E}_{\text {cell }}=-0.14$
since in (A) (B) (C) $E_{\text {cell }}$ is positive hence answer is (A) (B) (C).
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 $\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]^{3-}$

Ans. (A,B,D)
Sol.(A)
$\left[\mathrm{FeCl}_{4}\right]^{-}$
$\mathrm{Fe} \longrightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{6} 4 \mathrm{~s}^{2}$
$\mathrm{Fe}^{+3} \longrightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{5} 4 \mathrm{~s}^{0}$
$\mathrm{Cl}^{-}$is W.F.L. and does not pair up the unpaired electron of central metal atom.


(B)

## $\left[\mathrm{Co}(\mathrm{CO})_{4}\right]$

$\mathrm{Co} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{7} 4 \mathrm{~s}^{2}$
$\mathrm{Co}^{-1} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$
$\therefore \mathrm{Co}^{-}\left(\mathrm{d}^{10}\right)$ in $\left[\mathrm{Co}(\mathrm{CO})_{4}\right]^{-}$

$\left[\mathrm{CoCl}_{4}\right]^{2-}$


Tetrahedral
$\mathrm{Co} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{7} 4 \mathrm{~s}^{2}$
$\mathrm{Co}^{+2} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{7} 4 \mathrm{~s}^{0}$
$\mathrm{Cl}^{-}$is W.F.L. and does not pair up the unpaired electron of central metal atom.


Tetrahedral
(C)

## $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$

$\mathrm{Ni} \longrightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$
$\mathrm{Ni}^{0} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$

$\therefore \mathrm{Ni}\left(\mathrm{d}^{10}\right)$ in $\left[\mathrm{Ni}(\mathrm{CO})_{4}\right]$|  | $1 l$ | $1 /$ | $1 l$ | $1 l$ |
| :--- | :--- | :--- | :--- | :--- |
|  |  | $1 l$ |  |  |

$\left[\mathrm{Ni}(\mathrm{CN})_{4}\right]^{2-}$
$\mathrm{Ni} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{8} 4 \mathrm{~s}^{2}$

$\mathrm{Ni}^{+2} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{8} 4 \mathrm{~s}^{0}$
$\mathrm{CN}^{-}$is S.F.L. and pair up the unpaired electron of central metal atom.


## (D) $\left[\mathrm{Cu}(\mathrm{py})_{4}\right]^{+}$

$$
\mathrm{Cu} \longrightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{10} 4 \mathrm{~s}^{1}
$$

$$
\mathrm{Cu}^{+1} \rightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{10} 4 \mathrm{~s}^{0}
$$



## $\left[\mathrm{Cu}(\mathrm{CN})_{4}\right]^{3-}$

$\mathrm{Cu} \longrightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{10} 4 \mathrm{~s}^{1}$
$\mathrm{Cu}^{+1} \longrightarrow[\mathrm{Ar}] 3 \mathrm{~d}^{10} 4 \mathrm{~s}^{0}$
$\mathrm{CN}^{-}$is S.F.L. and pair up the unpaired electron of central metal atom.

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.

Ans. (A,B,D)
Sol. (A) $4 \mathrm{H}_{3} \mathrm{PO}_{3} \xrightarrow{\Delta} 3 \mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{PH}_{3}$ (correct)
(B) $\mathrm{H}_{3} \mathrm{PO}_{4}$ has " P " in its highest oxidation state, hence cannot act as a reducing agent (correct)
(C)

(D)


The hydrogen which is directly attached to phosphorous does not ionized in water.


SECTION-2 : (Maximum Marks : 12)

- 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 $\quad:+2$ 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 $4 \times 10^{2} \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$. At 298 K , for an aqueous solution of the acid the degree of dissociation of $\boldsymbol{\alpha}$ and the molar conductivity is $\mathbf{y} \times 10^{2} \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$. At 298 K , upon 20 times dilution with water, the molar conductivity of the solution becomes $3 \mathbf{y} \times 10^{2} \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$.
7. The value of $\alpha$ is $\qquad$ .

Ans. (0.21 or 0.22)

## Solution for Q. 7 \& Q. 8

Sol. $\mathrm{K}_{\mathrm{a}}=\frac{\Lambda_{\mathrm{m}}^{2} \mathrm{C}}{\Lambda_{\mathrm{m}}^{\circ}\left(\Lambda_{\mathrm{m}}^{\circ}-\Lambda_{\mathrm{m}}\right)}$
$\mathrm{K}_{\mathrm{a}}=\frac{\left(\mathrm{y} \times 10^{2}\right)^{2} \times \mathrm{C}}{4 \times 10^{2}\left(4 \times 10^{2}-\mathrm{y} \times 10^{2}\right)}=\frac{\left(3 \mathrm{y} \times 10^{2}\right)^{2} \times \frac{\mathrm{C}}{20}}{4 \times 10^{2}\left(4 \times 10^{2}-3 \mathrm{y} \times 10^{2}\right)}$
$\Rightarrow \frac{1}{(4-y)}=\frac{9}{20(4-3 y)} \Rightarrow y=\frac{44}{51}$
$\alpha=\frac{\frac{44}{51} \times 10}{4 \times 10^{2}}$
$\alpha=0.2156(\alpha=0.22$ or 0.21$)$
$y=0.86$
8. The value of $\mathbf{y}$ is $\qquad$ .
Ans. (0.86)

## Question Stem for Question Nos. 9 and 10

## Question Stem

Reaction of $\mathbf{x} \mathrm{g}$ of Sn with HCl quantitatively produced a salt. Entire amount of the salt reacted with $\mathbf{y} \mathrm{g}$ 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 $\mathbf{x}$ is $\qquad$ .
Ans. (3.57)
Sol. The value of $\mathbf{x}$ is


So to get 1.29 gm organic salt.
We have to form 0.01 mole salt.
So 0.01 mole nitrobenzene is required.
0.03 mole Sn is required.

So the amount of nitrobenzene $=0.01 \times 123=1.23 \mathrm{gm}$
the amount of Sn required $=0.01 \times 357=3.57 \mathrm{gm}$
Ans. 3.57 \& 1.23
10. The value of $\mathbf{y}$ is $\qquad$ .
Ans. (1.23)
Sol. The value of $\mathbf{y}$ is


So to get 1.29 gm organic salt.
We have to form 0.01 mole salt.
So 0.01 mole nitrobenzene is required.
0.03 mole Sn is required.

So the amount of nitrobenzene $=0.01 \times 123=1.23 \mathrm{gm}$
the amount of Sn required $=0.01 \times 357=3.57 \mathrm{gm}$
Ans. 3.57 \& 1.23

## 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 $\mathbf{x} \times 10^{-2}$ (consider complete dissolution of $\mathrm{FeCl}_{2}$ ). The amount of iron present in the sample of $\mathbf{y} \%$ 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 $\mathbf{x}$ is $\qquad$ .
Ans. (1.87 or 1.88)

## Solution for Q. 11 \& Q. 12

$\mathrm{Fe}+2 \mathrm{HCl} \longrightarrow \mathrm{FeCl}_{2}+\mathrm{H}_{2}$
x mole
x mole
$\mathrm{Fe}^{+2}+\mathrm{MnO}^{-}$
$\frac{\mathrm{x}}{10 \mathrm{~mole}}$
12.5 ml

10 mole

$$
0.03 \mathrm{M}
$$

$\mathrm{n}_{\mathrm{f}}=1$

$$
\mathrm{n}_{\mathrm{f}}=5
$$

$\frac{\mathrm{x}}{10}=\frac{12.5 \times 0.03 \times 5}{1000}$
$\mathrm{x}=0.01875(\mathrm{x}=1.88$ or 1.87$)$
wt of $\mathrm{Fe}=1.05 \mathrm{~g}$
$\% \mathrm{Fe}=\frac{1.05}{5.6} \times 100=18.75$
12. The value of $\mathbf{y}$ is $\qquad$ .
Ans. (18.75)

## SECTION-3 : (Maximum Marks : 12)

- 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 : $-1 \quad$ 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 :

|  | $\longrightarrow$ | (g) | $+\mathrm{H}^{\mathbf{*}}(\mathrm{g})$ | $\Delta \mathrm{H}^{\mathrm{o}}=105 \mathrm{kcal} \mathrm{~mol}^{-}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Cl}-\mathrm{C}$ |  | (g) | $+\mathrm{Cl}^{\bullet}(\mathrm{g})$ | $\Delta \mathrm{H}^{\circ}=58 \mathrm{kcal} \mathrm{mol}^{-1}$ |
| $\mathrm{H}_{3} \mathrm{C}-\mathrm{Cl}(\mathrm{g})$ |  | ${ }^{\bullet}$ (g) | $+\mathrm{Cl}^{\bullet}(\mathrm{g})$ | $\Delta \mathrm{H}^{\circ}=85 \mathrm{kcal} \mathrm{mol}^{-1}$ |
| $\mathrm{H}-\mathrm{Cl}(\mathrm{g})$ |  | H (g) | $+\mathrm{Cl}^{\bullet}(\mathrm{g})$ | $\Delta H^{\circ}=103 \mathrm{kcal} \mathrm{mol}^{-1}$ |

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 Molecule | Column K <br> BDE $\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ |
| :---: | :---: |
| (P) $\mathbf{H - C H}\left(\mathrm{CH}_{3}\right)_{2}$ | (i) 132 |
| (Q) $\mathrm{H}-\mathrm{CH}_{2} \mathrm{Ph}$ | (ii) 110 |
| (R) $\mathbf{H}-\mathrm{CH}=\mathrm{CH}_{2}$ | (iii) 95 |
| (S) $\mathrm{H}-\mathrm{C} \equiv \mathrm{CH}$ | (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, $\mathrm{R}-\mathrm{i}, \mathrm{S}$ - iv
(D) P - ii, Q - i, R - iv, S - iii

Ans. (A)
Sol. Most stability of radical, less is the bond energy
(P)

(Q) $\mathrm{Ph}-\mathrm{CH}_{2}-\mathrm{H} \longrightarrow \mathrm{Ph}-\mathrm{CH}_{2}+\mathrm{H}^{\bullet}$ Most stable due to resonance
(R) $\mathrm{CH}_{2}=\mathrm{CH}-\mathrm{H} \longrightarrow \mathrm{CH}_{2}=\mathrm{CH}+\mathrm{H}^{\bullet}$ (less stable)
(S)
 More \% S-Character decreases stability of free radical

Q require least BDE and S Required maximum BDE
Max BDE
So, Order of BDE $\mathrm{Q}<\mathrm{P}<\mathrm{R}<\mathrm{S}$
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 ${ }^{\circ} \mathrm{CH}_{3}$ 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 $\Delta \mathrm{H}^{\circ}=-25 \mathrm{kcal} \mathrm{mol}^{-1}$.

Ans. (D)
Sol. Initiation step is endothermic hence option (A) is wrong.
Propagation step involving ${ }^{\circ} \mathrm{CH}_{3}$ formation is endothermic hence option (B) is wrong.
Propagation step involving $\mathrm{CH}_{3} \mathrm{Cl}$ formation is exothermic hence option (C) is wrong.

## Reaction

$\mathrm{CH}_{4}+\mathrm{Cl}_{2} \longrightarrow \mathrm{CH}_{3}-\mathrm{Cl}+\mathrm{HCl}$
$\mathrm{CH}_{4} \longrightarrow \mathrm{CH}_{3}^{-}+\mathrm{H}^{\cdot} \quad \Delta \mathrm{H}=105 \mathrm{KCal} / \mathrm{mol}$
$\mathrm{Cl}_{2} \longrightarrow \mathrm{Cl}^{\circ}+\mathrm{Cl}^{\circ} \quad \Delta \mathrm{H}=58 \mathrm{KCal} / \mathrm{mol}$
$\mathrm{Cl}^{\circ}+\mathrm{CH}_{3}^{-} \longrightarrow \mathrm{CH}_{3}-\mathrm{Cl} \quad \Delta \mathrm{H}=-85 \mathrm{KCal} / \mathrm{mol}$
$\mathrm{Cl}^{-}+\mathrm{H}^{-} \longrightarrow \mathrm{HCl} \quad \Delta \mathrm{H}=-103 \mathrm{KCal} / \mathrm{mol}$
$\mathrm{CH}_{4}+\mathrm{Cl}_{2} \longrightarrow \mathrm{CH}_{3}-\mathrm{Cl}+\mathrm{HCl} \Delta \mathrm{H}=-25 \mathrm{KCal} / \mathrm{mol}$
Overall reaction is exothermic with $\Delta \mathrm{H}^{\circ}=-25 \mathrm{KCal} / \mathrm{mol}$, hence option (D) is correct.

## 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 $\mathbf{X}$, 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 $\mathbf{X}$ 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) $\mathrm{KFe}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$

Ans. (C)

Sol. $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right] \xrightarrow[\text { absence of air }]{\mathrm{FeSO}_{4}} \mathrm{~K}_{2} \mathrm{Fe}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$
White precipitate

$$
\text { air }
$$

$\stackrel{\text { air }}{\mathrm{Fe}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}}$
(Prussian Blue)
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) $\left[\mathrm{Fe}(\mathrm{NO})\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{2+}$

Ans. (D)
Sol. $\mathrm{FeSO}_{4} \xrightarrow[\substack{\text { slow and dition } \\ \text { of conc. } \mathrm{H}_{2} \mathrm{SO}_{4}}]{\mathrm{NaO}_{3}} \underset{\text { (Brown Ring Complex) }}{\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{NO}\right] \mathrm{SO}_{4}}$

## SECTION-4 : (Maximum Marks : 12)

- 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 $\qquad$ .

( $U$ : internal energy, $S$ : entropy, $p$ : pressure, $V$ : volume, $R$ : gas constant)
(Given: molar heat capacity at constant volume, $C_{V, \mathrm{~m}}$ of the gas is $\frac{5}{2} R$ )

Ans. (10)
14

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Sol. $\Delta \mathrm{U}_{\mathrm{I}}=\mathrm{nC}_{\mathrm{v}, \mathrm{m}} \Delta \mathrm{T}=\mathrm{W}_{\mathrm{I}}\left\{\mathrm{q}_{\mathrm{I}}=0\right\}$
$-1800 \mathrm{R}=1 \times \frac{5 \mathrm{R}}{2} \times \Delta \mathrm{T}=\Delta \mathrm{T}=-720 \mathrm{~K}$
$\mathrm{T}_{2}=180 \mathrm{~K}$
$\mathrm{W}_{\mathrm{II}}=\mathrm{W}_{\mathrm{I}}=-1800 \mathrm{R}=-1 \times \mathrm{R} \times 180 \ln \left(\frac{\mathrm{~V}_{3}}{\mathrm{~V}_{2}}\right)$
$\ln \left(\frac{\mathrm{V}_{3}}{\mathrm{~V}_{2}}\right)=10 \Rightarrow 10$
18. Consider a helium ( He ) atom that absorbs a photon of wavelength 330 nm . The change in the velocity (in $\mathrm{cm} \mathrm{s}^{-1}$ ) 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 $\mathrm{He}=4 \mathrm{~g} \mathrm{~mol}^{-1}$ )
Ans. (30)
Sol. $\lambda=\frac{\mathrm{h}}{\mathrm{p}} \Rightarrow \mathrm{p}=\frac{6.6 \times 10^{-34}}{330 \times 10^{-9}}=\frac{4 \times 10^{-3}}{6 \times 10^{23}} \times \mathrm{v}(\mathrm{p}=\mathrm{m} \times \mathrm{v})$
$\mathrm{v}=0.3 \mathrm{~m} / \mathrm{s}=30 \mathrm{~cm} / \mathrm{s}$
19. Ozonolysis of $\mathrm{ClO}_{2}$ produces an oxide of chlorine. The average oxidation state of chlorine in this oxide is $\qquad$ .

Ans. (6)
Sol. $2 \mathrm{ClO}_{2}+2 \mathrm{O}_{3} \longrightarrow \mathrm{Cl}_{2} \mathrm{O}_{6}+2 \mathrm{O}_{2}$

## $\mathrm{Cl}_{2} \mathrm{O}_{6}$

$$
2 x+6(-2)=0
$$

$$
x=+6
$$

Average oxidation state of Cl in $\mathrm{Cl}_{2} \mathrm{O}_{6}$ is 6 .

