## INDIAN ASSOCIATION OF CHEMISTRY TEACHERS

NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) 2017-18

## Examination Date : 26-11-2017

## Q. PAPER CODE: C321

HBCSE Olympiad (STAGE - 1)
Write the question paper code mentioned above on YOUR answer sheet (in the space provided), otherwise your answer sheet will NOT be assessed. Note that the same Q. P. Code appears on each page of the question paper.

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1. At constant $T$ and $P, 5.0 \mathrm{~L}$ of $\mathrm{SO}_{2}$ are reacted with 3.0 L of $\mathrm{O}_{2}$ according to the following equation $2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{SO}_{3}(\mathrm{~g})$
The volume of the reaction mixture at the completion of the reaction is
(A) 0.5 L
(B) 8.0 L
(C) 5.5 L
(D) 5 L

Ans. (C)

$$
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{SO}_{3}(\mathrm{~g})
$$

Sol. Initial volume $5 \mathrm{~L} \quad 3 \mathrm{~L} \quad 0$
Volume after $0+(3-2.5)+5=5.5 \mathrm{~L}$ reaction $=0.5$
2. The following disaccharide is made up of

(A) D-aldose and D-ketose
(B) L-aldose and L-ketose
(C) D-aldose and L-ketose
(D) L-aldose and D-ketose

Ans. (D)

Sol.

3. One mode of 4-nitrocatechol (4-nitro-1,2-dhydroxybenzene) on treatment with an excess of NaH followed by one mole of methyl iodide gives-
(A) 4-nitro-1, 2-diamethox ybenzene
(B) 4-nitro-5methy-1, 2-dimethox ybenzene
(C) 2-methox y-5 nitrophenol
(D) 2-methoxy-4nitrophenol

Ans. (D)

Sol.

4. The colour changes of an indicator HIn in acid base titrations is given below
$\mathrm{HIn}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{In}^{-}(\mathrm{aq})$
Colour X
Colour Y
Which of the following statements is correct?
(A) In a strong alkaline solution colour $Y$ will be observed
(B) In a strong acidic solution colour Y will be observed
(C) Concentration of $\mathrm{in}^{-}$is higher than that of HIn at the equivalence point
(D) In a strong alkaline solution colour X is observed

Ans. (A)
Sol. It is an acidic indicator therefore will remain in ionized form in strong alkaline solution (opposite ion effect).
5. The table below gives the results of three titrations carried out with 0.200 M HCl to determine the molarity of a given NaOH solution using phenolphthalein as indicator. NaOH was taken in the burette and HCl was taken in a conical flask for the titrations

| Titration No. | $\mathrm{V}_{\mathrm{HCl}(\mathrm{mL})}$ | $\mathrm{V}_{\mathrm{NaOH}(\mathrm{mL})}$ | $\mathrm{M}_{\mathrm{NaOH} \mathrm{moldm}^{-3}}$ |
| :--- | :--- | :--- | :--- |
| I | 21.4 | 19.3 | 0.222 |
| II | 18.6 | 16.8 | 0.221 |
| III | 22.2 | 21.1 | 0.210 |

The actual molarity of the prepared NaOH solution was $0.220 \mathrm{~mol} \mathrm{dm}^{-3}$. Which among the following could be the reason for the wrong value obtained in titration III?
(A) Number of drops of phenolphthalein added to the titration flask was more in this titration
(B) The concentration of HCl was wrongly used as 0.250 M for the calculation of $\mathrm{M}_{\mathrm{NaOH}}$
(C) A few drops of NaOH solution were spilled outside the titration flask during titration
(D) A few drops of the neutralized solution from titration II were left behind in the flask

Ans. (C)

Sol.

$\left[\mathrm{OH}^{-}\right]=\frac{\mathrm{n}_{\mathrm{OH}^{-}}}{\mathrm{V}_{\mathrm{OH}^{-}}}=\frac{\mathrm{n}_{\text {acid }}}{\mathrm{V}_{\mathrm{NaOH}}}=\frac{[\mathrm{HCl}] \mathrm{V}_{\mathrm{HCl}}}{\mathrm{V}_{\mathrm{NaOH}}}=0.21 \mathrm{M}<0.220$
6 The solution with pH value close to 1 is
(A) 10 mL of $0.1 \mathrm{M} \mathrm{HCl}+90 \mathrm{~mL}$ of 0.1 M NaOH
(B) 55 mL of $0.1 \mathrm{M} \mathrm{HCl}+45 \mathrm{~mL}$ of 0.1 M NaOH
(C) 75 mL of $0.2 \mathrm{M} \mathrm{HCl}+25 \mathrm{~mL}$ of 0.2 M NaOH
(D) 75 mL of $0.2 \mathrm{M} \mathrm{HCl}+25 \mathrm{~mL}$ of 0.1 M NaOH

Ans. (C)
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Sol. $\left[\mathrm{H}^{+}\right]=\frac{15-5}{75+25}=10^{-1} \mathrm{M}$
or $\mathrm{pH}=1$
7. The most basic nitrogen in the following compound is

(A) I
(B) II
(C) III
(D) IV

Ans. (C)

Sol.


Lone pair of III is localised therefore it is most basic.
8. For the reaction $\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightarrow$ the rate expression is $-\mathrm{d}\left[\mathrm{NH}_{3}\right] / \mathrm{dt}=\mathrm{k}\left[\mathrm{H}_{2}\right]\left[\mathrm{N}_{2}\right]$

The correct statement is
I. The reaction is not elementary
II. The reaction is of second order
III. $-\mathrm{d}\left[\mathrm{H}_{2}\right] / \mathrm{dt}=-\mathrm{d}\left[\mathrm{NH}_{3}\right] / \mathrm{dt}$
(A) II only
(B) I and II
(C) II and III
(D) I, II and III

Ans. (B)
Sol. $r=-\frac{d\left[\mathrm{~N}_{2}\right]}{\mathrm{dt}}=-\frac{1}{3} \frac{\mathrm{~d}\left[\mathrm{H}_{2}\right]}{\mathrm{dt}}=\frac{1}{2} \frac{\mathrm{~d}\left[\mathrm{NH}_{3}\right]}{\mathrm{dt}}$
9. Which of the following is correct?

A liquid with
(A) low vapour pressure will have a low surface tension and high boiling point
(B) high vapour pressure will have high intermolecular forces and high boiling point
(C) low vapour pressure will have high surface tension and high boiling point
(D) low vapour pressure will have low surface tension and low boiling point

Ans. (C)
Sol. A liquid with low vapour pressure (less volatile) will have a high surface tension and high boiling point
10. At $25^{\circ} \mathrm{C}$, nitrogen exists as $\mathrm{N}_{2}$ and phosphorous exists as $\mathrm{P}_{4}$ because
(A) $\mathrm{N}_{2}$ has valence electrons only in bonding and nonbonding orbitals, while P has valence electrons in both bonding and antibonding orbitals
(B) higher electronegativity of N favours formation of multiple bonds
(C) bigger size of P does not favour multiple bonds
(D) P has preference to adapt structures with small bond angles

Ans. (C)
Sol. Nitrogen forms multiple bonds due to small size.
11. The product of the following reaction is

(A)

(B)

(C)

(D)


Ans. (A)

Sol.



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12. Three samples of 100 g of water (samples I, II and III), initially kept at 1 atm pressure and 298 K were given the following treatments.
Sample I was heated to 320 K and cooled to 298 K
Sample II was heated to 300 K , cooled to 273 K and heated to 298 K
Sample III was heated to 373 K and cooled to 298 K
At the end of these processes, the internal energy of
(A) III is the highest
(B) II is the highest
(C) I and III are the same, II is lower than that of I and III
(D) I, II and III are the same

Ans. (D)
Sol. Internal energy change is a state function.
13. For the reaction
$5 \mathrm{Br}^{-}(\mathrm{aq})+\mathrm{BrO}_{3}^{-}(\mathrm{aq})+6 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow 3 \mathrm{Br}_{2}(\mathrm{aq})+3 \mathrm{H}_{2} \mathrm{O}$ ( I$)$
the rate expression was found to be $-\mathrm{d}\left[\mathrm{BrO}_{3}\right] / \mathrm{dt}=\mathrm{k}[\mathrm{Br}]\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{BrO}_{3}^{-}\right]$
Which of the following statements is/are correct?
I. Doubling the initial concentration of all the reactants will increase the reaction rate by a factor of 8
II. Unit of rate constant of the reaction in a buffer solution is $\mathrm{min}^{-1}$
III. Doubling the concentration of all the reactants at the same time will increase the reaction rate by a factor of 16
IV. rate of conversion of $\mathrm{BrO}_{3}^{-}$and rate of formation of $\mathrm{Br}^{-}$are the same
(A) I and II
(B) II and III
(C) II and IV
(D) III only

Ans. (D)
Sol. $\quad r=-\frac{\mathrm{d}\left[\mathrm{BrO}_{3}^{-}\right]}{\mathrm{dt}}=\frac{1}{3} \frac{\mathrm{~d}\left[\mathrm{Br}_{2}\right]}{\mathrm{dt}}$

$$
\begin{gathered}
\mathrm{r}^{\prime}=\mathrm{K}[2 \mathrm{Br}]\left[2 \mathrm{H}^{+}\right]^{2}\left[2 \mathrm{BrO}_{3}^{-}\right] \\
= \\
=16 \mathrm{r}
\end{gathered}
$$

14. In the Lewis structure of ozone $\left(\mathrm{O}_{3}\right)$, the formal charge on the central oxygen atom is
(A) +1
(B) -1
(C) 0
(D) -2

Ans. (A)
Sol.

15. Which of the following on treatment with hot concentrated acidified $\mathrm{KMnO}_{4}$ will give 2-methylhexane -1,6-dioic acid as the only organic product?
(A)

(B)

(C)

(D)


Ans. (C)

Sol.


2-Methylhexane-1,6-dioic acid
16. For the following spontaneous process
$\mathrm{H}_{2} \mathrm{O}_{(I)} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{s})}$ at 268 K , which of the following is true?
(A) $\Delta S_{\text {sys }}<0$
(B) $\Delta \mathrm{S}_{\text {sys }}>0$
(C) $\Delta \mathrm{S}_{\text {surr }}<0$
(D) $\Delta S_{\text {sys }}=-\Delta S_{\text {surr }}$

Ans. (A)
Sol. Liquid is converting into solid also in the process heat is released therefore $\Delta \mathrm{S}_{\text {sys }}<0$
also $\Delta \mathrm{S}_{\text {total }}>0$
17. Lithium oxide ( $\mathrm{Li}_{2} \mathrm{O}$; molar mass $=30 \mathrm{~g} \mathrm{~mol}^{-1}$ ) is used in space shuttles to remove water vapour according to the following reaction
$\mathrm{Li}_{2} \mathrm{O}_{(\mathrm{s})}+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow 2 \mathrm{LiOH}_{(\mathrm{s})}$
If 60 kg of water and 45 kg of $\mathrm{Li}_{2} \mathrm{O}$ are present in a shuttle
I . water will be removed completely
II. $\mathrm{Li}_{2} \mathrm{O}$ will be the limiting reagent
III. 100 kg of $\mathrm{Li}_{2} \mathrm{O}$ will be required to completely remove the water present
IV. 27 kg of water will remain in the shuttle at the end of the reaction
(A) II only
(B) II and IV
(C) III and IV
(D) II, III

Ans. (D)
Sol.

18. The order of enol content in the following molecule is

(a)

(b)

(c)

(d)
(A) a $>$ d $>$ c $>$ b
(B) a $>$ c $>$ d $>$ b
(C) a $>$ c $>$ b $>$ d
(D) a $>$ b $>$ c $>$ d

Ans. (A)

Sol. (a)


Aromatic
(d)
 Active methylene group
(c)

(b)

19. The product of the following reaction is

(i) $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{MgBr}$, dry ether
(ii) $\mathrm{H}_{3} \mathrm{O}^{+}$
(iii) $\mathrm{PCl}_{5}$
(iv) $\mathrm{NaOC}_{2} \mathrm{H}_{5} / \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$
(A)

(B)

(C)

(D)


Ans. (C)

Sol.


20. At constant volume, 6.0 mol of $\mathrm{H}_{2}$ gas at $0^{\circ} \mathrm{C}$ and 100 kPa was heated to 250 kPa . The molar heat of $\mathrm{H}_{2}$ at constant pressure $\left(\mathrm{C}_{\mathrm{P}}\right)=28.9 \mathrm{~J} \mathrm{~mol}^{-1}$. (assume that the heat capacity values do not change with temperature). The final temperature of the $\mathrm{H}_{2}$ gas and the change in entropy of the process are
(A) $273^{\circ}{ }^{\mathrm{C}}$ and $113 \mathrm{~kJ} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$
(B) $410^{\circ} \mathrm{C}$ and $158.8 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$
(C) $682.5^{\circ} \mathrm{C}$ and $113 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$
(D) $682.5 \mathrm{~K}^{\text {and }} 113 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$

Ans. (D)
Sol. $\frac{P_{1}}{T_{1}}=\frac{P_{2}}{T_{2}}$

$$
\begin{aligned}
& \frac{100}{273}=\frac{250}{T_{2}} \quad \text { or } T_{2}=682.5 \mathrm{~K} \\
& \begin{aligned}
\Delta S=n C_{V} & \ln \frac{T_{2}}{T_{1}} \\
& =2.303 \mathrm{n}\left(\mathrm{C}_{P}-\mathrm{R}\right) \log \frac{T_{2}}{T_{1}} \\
& =2.303 \times 6 \times(28.9-8.314) \log \frac{682.5}{273} \\
& \approx 113 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~mol}^{-1}
\end{aligned}
\end{aligned}
$$

21. The cubic unit cell of an oxide of metals $A$ and $B$ is as given below, in which oxygen. $A$ and $B$ are represented by open circles, crossed circles and dark circle respectively.


The formula of the oxide can be deduced as
(A) $\mathrm{AB}_{8} \mathrm{O}_{12}$
(B) ABO
(C) $\mathrm{ABO}_{6}$
(D) $\mathrm{ABO}_{3}$

Ans. (D)
Sol. Number of atoms of $A /$ unit cell $=1$
Number of atoms of $B /$ unit cell $=8 \times \frac{1}{8}=1$
Number of atom of $0 /$ unit cell $=12 \times \frac{1}{4}=3$
So, the formula of the oxide is $\mathrm{ABO}_{3}$.
22. When a medal is electroplated with silver (Ag)
(A) The medal is the anode
(B) Ag metal is the cathode
(C) The solution contains $\mathrm{Ag}^{+}$ions
(D) The reaction at the anode is $\mathrm{Ag}^{+}+\mathrm{e}^{-} \longrightarrow \mathrm{Ag}$

Ans. (C)
Sol. For electroplating of metal with silver
Cathode $\rightarrow$ Metal
Anode $\rightarrow$ Ag
Solution $\rightarrow$ Electrolyte containing $\mathrm{Ag}^{+}$
23. The energy of an electron in Bohr's orbit of hydrogen atom is -13.6 eV . The total electronic energy of a hypothetical' He atom is which there are no electron- electron repulsions is
(A) 27.2 eV
(B) -27.2 eV
(C) -108.8 eV
(D) $108 . \mathrm{eV}$

Ans. (C)
Sol. Electronic energy per electron $=-13.6 \times 4 \mathrm{eV}$
Total Electronic energy $=-13.6 \times 4 \times 2=-108.8 \mathrm{eV}$
24. Iodine is a solid and sublimes at ordinary temperature. This is because of :
(A) weak I-I bonds
(B) strong I-I bonds
(C) lone pair-bond pair repulsions
(D) weak van der Waals forces between $\mathrm{I}_{2}$ molecules

Ans. (D)
Sol. $\quad \mathrm{I}_{2}$ is solid \& sublimes at ordinary temperature because of weak vander wal's force between $\mathrm{I}_{2}$ molecules.
25. The equilibrium constant of the following isomerisation reaction at 400 K and 298 K are 2.07 and 3.42 respectively.
cis-butene $\underset{\mathrm{k}_{-1}}{\stackrel{\mathrm{k}_{1}}{\rightleftharpoons}}$ trans-butene
Which of the following is/are correct?
I. The reaction is exothermic
II. The reaction is endothermic
III. At $400 \mathrm{~K} 50 \%$ of cis-butene and $50 \%$ of trans-butene are present of equilibrium
IV. Both at 298 K and $400 \mathrm{~K}, \mathrm{k}_{1}=\mathrm{k}_{-1}$
(A) I and IV
(B) II and IV
(C) I and III
(D) I only

Ans. (D)
Sol. As on T increase, $\mathrm{K}_{\text {eq }}$ is increasing, Reaction is exothermic.

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26. Which of the following will not give a straight line plot for an ideal gas ?
(A) V vs T
(B) T vs P
(C) V vs I/P
(D) V vs I/T

Ans. (D)
Sol. $\quad P V=n R T$
$V=\frac{n R T}{P}$
$\mathrm{V} \mathrm{v} / \mathrm{s} \frac{1}{\mathrm{~T}}$ will not be a straight line.
27. Levonorgestrel is a commonly used contraceptive. The number of chiral centres present in this molecule is :


Levonorgestrel
(A) 4
(B) 5
(C) 6
(D) 7

Ans. (C)
Sol. Number of chiral centres are 6.


Levonorgestrel
28. Which of the following ethers cannot be prepared by Williamson Synthesis ?
(A)

(B)

(C)

(D)


Ans. (B)
Sol. $\mathrm{PhO}^{-}+\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{X} \longrightarrow$ No Reaction
Or $\quad\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CO}^{-}+\mathrm{Ph}-\mathrm{X} \longrightarrow$ No Reaction
Hint : $\quad\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C}-\mathrm{X}$ and $\mathrm{Ph}-\mathrm{X}$ do not react by $\mathrm{SN}^{2}$ reaction.
29. IUPAC name of complex ion $\left[\mathrm{CrCl}_{2}(\mathrm{ox})_{2}\right]^{3-}$ is
(A) dichlorodioxalatochromium (III)
(B) dioxalatodichlorochromate(III)
(C) dichlorodioxalatochromate(III)
(D) bisoxalaeodichlorochromate(III)

[^0]
## Ans. (C)

Sol. IUPAC name is dichlorodioxalatochromate (III)
30. Sodium azide $\left(\mathrm{NaN}_{3}\right)$ is used in airbag of cars. This is safety device with inflates on an impact according to the reaction $\quad 2 \mathrm{NaN}_{3} \rightarrow 2 \mathrm{Na}+3 \mathrm{~N}_{2}$
An air bag of a particular car can be filled with 44.8 L of gas at STP. The mass (g) of $\mathrm{NaN}_{3}$ required to fill this airbag completely at 298 K and 1 atm. pressure is :
(A) 87
(B) 130
(C) 84
(D) 100

Ans. (A)
Sol. As the maximum volume of airbag will remain same irrespective of temperature hence to fill me bag at 298 K .
$\mathrm{V}=44.8 \mathrm{~L}$
$\mathrm{T}=298 \mathrm{~K}$
$\mathrm{P}=1 \mathrm{~atm}$
$\mathrm{n}\left(\right.$ of $\left.\mathrm{N}_{2}\right)=1.83$
moles of $\mathrm{NaN}_{3}$ required $=\frac{2}{3} \times 1.83=1.22$ mole
mass of $\mathrm{NaN}_{3}$ required $=1.22 \times 65=79.4 \mathrm{~g}$
$\Rightarrow$ So it should be bonus.
Comment : If we consider that airbag will contain same mole at both temperature ( $273 \mathrm{~K} \& 298 \mathrm{~K}$ )
(i.e. assuming volume expansion at bag with temperature)

So moles of $\mathrm{N}_{2}$ at STP $=2(\mathrm{~T}=273 \mathrm{~K})$
Moles of $\mathrm{N}_{2}$ at $298 \mathrm{~K} \& 1 \mathrm{~atm}=2$
Moles of $\mathrm{NaN}_{3}$ reqd. $=\frac{2}{3} \times 2=\frac{4}{3}$
Mass of $\mathrm{NaN}_{3}$ required $=\frac{4}{3} \times 65 \simeq 84 \mathrm{~g}$.
So (A) can be considered with the above unjustified assumptions.
31. Which of the following mixtures of water and $\mathrm{H}_{2} \mathrm{SO}_{4}$ would have mass percentage of $\mathrm{H}_{2} \mathrm{SO}_{4}$ close to 30 ?
(A) $30 \mathrm{~g} \mathrm{H}_{2} \mathrm{SO}_{4}+100 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}$
(B) 1 mol of $\mathrm{H}_{2} \mathrm{SO}_{4}+2 \mathrm{~mol}$ of $\mathrm{H}_{2} \mathrm{O}$
(C) 1 mol of $\mathrm{H}_{2} \mathrm{SO}_{4}+200 \mathrm{~g}$ of $\mathrm{H}_{2} \mathrm{O}$
(D) $0.30 \mathrm{~mol} \mathrm{H}_{2} \mathrm{SO}_{4}+0.70 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}$

Ans. (C)
Sol. Mass percentage of $\mathrm{H}_{2} \mathrm{SO}_{4}=\frac{98}{298} \times 100=32.88$
Closest to 30.
32. In chlorides, the common oxidation states of aluminium and thallium are +3 and +1 respectively because.
(A) $\mathrm{Tl}-\mathrm{Cl}$ bond is ionic and $\mathrm{Al}-\mathrm{Cl}$ bond is covalent
(B) 6 s electrons of Tl are bound more strongly than the 3 s electron of Al
(C) $\mathrm{TI}-\mathrm{Cl}$ bond is stronger than $\mathrm{Al}-\mathrm{Cl}$ bond
(D) 3 s electrons of Al are bond strongly than the 6 s electrons of TI

Ans. (B)
Sol. 6s electrones of Tl are bond more strongly than 3s electrons of Al. (inert pair effect) Also Ionisation energy of $\mathrm{Tl}>$ lonisation energy of Al .

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33．In the given compound the order of case with which hydrogen atom can be abstracted from carbons I to VI is ：

（A） I $>$ VI $>$ IV $=$ V $>$ I $>$ III
（B） II $>$ I $>$ VI $>$ III $>$ IV $=$ V
（C） II $>$ I $>$ III $>$ VI $>$ IV $=$ V
（D） IV $>$ II $>$ I $>$ III $>$ IV $=$ V

Ans．（B）
Sol．Breaking of $\mathrm{C}-\mathrm{H}$ bond is inversely related to stability of intermediate free radical．

（Stability order of free radical）

## Use the table given below to answer questions 34 and 35

| Reaction | $\mathrm{E}_{0} / \mathrm{V}$ |
| :--- | :--- |
| $\mathrm{Ag} \rightarrow \mathrm{Ag}^{+}+\mathrm{e}^{-}$ | -0.80 |
| $\mathrm{Cr}^{3+}+3 \mathrm{e}^{-} \rightarrow 3 \mathrm{Cr}$ | -0.74 |
| $\mathrm{Zn}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Zn}$ | -0.76 |
| $\mathrm{I}_{2}(\mathrm{~s})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{I}^{-}$ | 0.54 |
| $\mathrm{Co}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Co}$ | -0.28 |
| $\mathrm{Ni}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ni}$ | -0.26 |

34．The best reducing agent among the following is
（A） $\mathrm{Ag}^{+}$
（B） $\mathrm{Zn}^{2+}$
（C） $\mathrm{Cr}^{3+}$
（D） $\mathrm{I}^{-}$

Ans．（D）
Sol． $\mathrm{Ag}^{+}, \mathrm{Zn}^{2+}, \mathrm{Cr}^{3+}$ are not reducing agents．
$I^{-}$Is a reducing agent．

35． E o of the given cell is ：
$\mathrm{NI}\left|\left(\mathrm{Ni}^{+2}, 1.0 \mathrm{M}\right)\right|\left|\left(\mathrm{Co}^{+2}, 1.0 \mathrm{M}\right)\right| \mathrm{Co}$
（A）+0.02 V
（B）-0.02 V
（C）-0.54 V
（D）+0.54 V

Ans．（B）
Sol． $\mathrm{E}^{\circ}{ }_{\text {cell }}=\mathrm{E}^{\circ}{ }_{\text {cathode（RP）}}-\mathrm{E}^{\circ}{ }_{\text {anode（RP）}}$
$=\mathrm{E}^{\circ} \mathrm{Co}^{+2} / \mathrm{Co}-\mathrm{E}^{0} \mathrm{Ni}^{+2} / \mathrm{Ni}$
$=-0.28-(-0.26)=-0.02 \mathrm{~V}$
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36. Which of the following is not a pair of a Lewis acid and a Lewis base ?
(A) $\mathrm{H}^{+},\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)_{2} \mathrm{O}$
(B) $\mathrm{H}_{2} \mathrm{O}, \mathrm{AlCl}_{3}$
(C) $\mathrm{Fe}^{3+}, \mathrm{CO}$
(D) $\mathrm{SiF}_{4}, \mathrm{BF}_{3}$

Ans. (D)
Sol. Both $\mathrm{SiF}_{4} \& \mathrm{BF}_{3}$ are both lewis acids.
37. The type of isomerism that $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Br}_{2} \mathrm{Cl}$ can exhibit is/are
(A) geometric and ionisation
(B) ionisation
(C) Optical and ionisation
(D) Optical, ionisation and geometric

Ans. (A)
Sol. It can exhibit geometric \& ionisation.
38. Pyrethrins are produced in chrysanthemum flowers and used as insecticides.

Structure of pyrethrin I is given below


Pyrethrin I (molar mass $=32.8 \mathrm{~g} / \mathrm{mol})$
The volume of $0.05 \mathrm{~mol} \mathrm{dm}^{3}$ bromine water that would with 500 mg sample of Pyrethrin I is
(A) $12.2 \mathrm{~cm}^{3}$
(B) $122 \mathrm{dm}^{3}$
(C) $122 \mathrm{~cm}^{3}$
(D) $1.31 \times 10^{3} \mathrm{~cm}^{3}$

Ans. (C)
Sol. Total position where Bromine water can attack is four.
39. Coniferyl alcohol is isolated from pine trees. The following observations were made about this alcohol.
I. It forms methylated product with Mel in presence of base
II. One equivalent of coniferyl alcohol reacts with two equivalents of benzoyl chloride
III. Upon ozonolysis, coniferyl alcohol gives a product 'Y' (M.F $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2}$ ).
(A)

(B)

(C)

(D)


Ans. (D)

Sol.



40. Which of the following represents a polymer of prop-2-en-l-ol ?
(A)

(B)

(C)

(D)


Ans. (B)
Sol.

41. A 500 mL glass flask is filled at 298 K and 1 atm, pressure with three diatomic gases $\mathrm{X}, \mathrm{Y}$ and Z . The initial volume ratio of the gases before mixing was $5: 3: 1$. The density of the heaviest gas in the mixture is not more than 25 times that of the lightest gas. When the mixture was heated, vigorous reactions take place between $X$ and $Y$ and $X$ and $Z$ in which all the three gases were completely used up.

The gases $\mathrm{X}, \mathrm{Y}, \mathrm{Z}$ respectively are
(A) $\mathrm{H}_{2}, \mathrm{O}_{2}, \mathrm{~N}_{2}$
(B) $\mathrm{H}_{2}, \mathrm{O}_{2}, \mathrm{Cl}_{2}$
(C) $\mathrm{H}_{2}, \mathrm{~F}_{2}, \mathrm{O}_{2}$
(D) $\mathrm{O}_{2}, \mathrm{H}_{2}, \mathrm{~F}_{2}$

Ans. (C)
Sol. According to given data.
Mole ratio of gas $x, y, z$ are $5: 3: 1$
$\rightarrow$ As given in the question that the density of heaviest gas in the mixture is not more then 25 times that of lightest gas. Hence gas mix should be $\mathrm{H}_{2}, \mathrm{~F}_{2}, \mathrm{O}_{2}$
$\rightarrow x=H_{2}, \quad y=F_{2}, \quad z=O_{2}$

| $\mathrm{H}_{2}+\mathrm{F}_{2} \longrightarrow 2 \mathrm{HF}$ | $\mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow$ | $\mathrm{H}_{2} \mathrm{O}$ |  |
| :--- | :--- | :--- | :--- |
| 5 a | 3 a | - | 2 a |
| 2 a | - | 6 a | - |
| 2 a |  |  |  |
| 2 |  |  |  |

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42. The reaction $X+Y \longrightarrow Z$ is first oder with respect to $X$ and second order with respect to $Y$. The initial rate of formation of $Z=R \mathrm{~mol} \mathrm{dm}{ }^{3} \mathrm{sec}^{-1}$ when $[X]_{0}$ and $[Y]_{0}$ are $0.40 \mathrm{~mol} \mathrm{dm}^{-3}$ and $0 . \mathrm{mol}$ $\mathrm{dm}^{3}$ respectively. If $[X]_{0}$ is halved and $[Y]_{0}$ is doubled, the value of the initial rate would become
(A) $4 R$
(B) $R / 4$
(C) $R$
(D) $2 R$

Ans. (D)

$$
\text { Sol. } \quad X+Y \longrightarrow Z
$$

$(\text { Rate })_{1}=\mathrm{K}[\mathrm{X}][\mathrm{Y}]^{2}$
$(\text { Rate })_{2}=K\left[\frac{X}{2}\right][2 Y]^{2}$
$\frac{(\text { Rate })_{1}}{(\text { Rate })_{2}}=\frac{1}{2} \quad(\text { Rate })_{2}=2(\text { Rate })_{1}=2 R$
43. Which one of the following statements is not correct about glucose ?
(molar mass of glucose $=180 \mathrm{~g} \mathrm{~mol}^{-1}$ )
(A) An aqueous 0.25 M solution of glucose is prepared by dissolving 45 g of glucose in water to give $1000 \mathrm{~cm}^{3}$ of solution
(B) 1.00 mmol glucose has a mass of 180 mg
(C) 90.0 g glucose contain $1.8 \times 10^{22}$ atoms of carbon
(D) $100 \mathrm{~cm}^{3}$ of a 0.10 M solution contains 18 g of glucose

Ans. (C) \& (D)
Sol. (A) $\mathrm{W}_{\text {glucose }}=0.25 \times 10 \times 180=45 \mathrm{~g}$
(B) $\mathrm{W}_{\text {glucose }}=1 \mathrm{mmole} \times 180=180 \mathrm{mg}$
(C) No. of C -atoms $=\frac{90}{180} \times \mathrm{N}_{\mathrm{A}} \times 6=18 \times 10^{23}$
(D) $\mathrm{W}_{\text {glucose }}=100 \times 0.1 \times 10^{-3} \times 180=1.8 \mathrm{~g}$

Hence C \& D both are in correct
44. The van der Waals equation for one mole of a real gas can be written as
$\left(P+a / V^{2}\right)(V-b)=R T$. For the gases $\mathrm{H}_{2}, \mathrm{NH}_{3}$, and $\mathrm{CH}_{4}$, the value of 'a' (bar $\mathrm{L}^{-2} \mathrm{~mol}^{-2}$ ) are $0.2453,4.170$ and 2.253 respectively.
Which of the following can be inferred from the 'a' values ?
(A) $\mathrm{NH}_{3}$ can be most easily liquified
(B) $\mathrm{H}_{2}$ can be most easily liquified
(C) value of 'a' for $\mathrm{CH}_{4}$ is less than that of $\mathrm{NH}_{3}$ because it has the lower molar mass
(D) intermolecular forces are the strongest in hydrogen

Ans. (A)
Sol. van der Wall's constant 'a' gives information about force of attraction between gaseous molecules.. Higher the value of 'a' higher will be force of attraction, and easier the liquefaction of gas.
Order of intermolecular force of attraction $=\mathrm{H}_{2}<\mathrm{CH}_{4}<\mathrm{NH}_{3}$

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45. Terpinen-4-ol is an active ingredient in tea tree oil has the following structure


The correct observations for terpinen-4-ol is/are
I. It rotates the plane of plane polarized light.
II. It reacts with Baeyer's reagent to form form a triol
III. On reaction with NaBr and $\mathrm{H}_{2} \mathrm{SO}_{4}$, it gives form a diobromo compound
IV. On ozonolysis it gives a compound with molecular formula $\mathrm{C}_{10} \mathrm{H}_{18} \mathrm{O}_{3}$
(A) I, II, III and IV
(B) I, III and IV
(C) II and III
(D) III and IV

Ans. (A)
Sol. (I) Terpinen-4-ol is an optically active molecule because it is chiral molecule
(II)

(III)

(IV)

46. The correct order of the ability of the leaving group is
(A) $\mathrm{OCOC}_{2} \mathrm{H}_{5}>\mathrm{OC}_{2} \mathrm{H}_{5}>\mathrm{OSO}_{2} \mathrm{Et}>\mathrm{OSO}_{2} \mathrm{CF}_{3}$
(B) $\mathrm{OC}_{2} \mathrm{H}_{5}>\mathrm{OCOC}_{2} \mathrm{H}_{5}>\mathrm{OSO}_{2} \mathrm{CF}_{3}>\mathrm{OSO}_{2} \mathrm{Me}$
(C) $\mathrm{OSO}_{2} \mathrm{CF}_{3}>\mathrm{OSO}_{2} \mathrm{Me}>\mathrm{OCOC}_{2} \mathrm{H}_{5}>\mathrm{OC}_{2} \mathrm{H}_{5}$
(D) $\mathrm{OCOC}_{2} \mathrm{H}_{5}>\mathrm{OSO}_{3} \mathrm{CF}_{3}>\mathrm{OC}_{2} \mathrm{H}_{5}>\mathrm{OSO}_{2} \mathrm{Me}$

Ans. (C)
Sol. Weaker bases are better leaving group.

47. Metal ' M ' forms a carbonly compound in which it is present in its lower valance state. Which of the following bonding is possible in this metal carbonyl ?
(A)

(B)

(C)

(D)


Ans. (B)
Sol. Bonding in metal carbonyl

$\pi$-bond $\rightarrow$ filled d-orbitel of metal and empty $\pi^{*}$ molecular orbital of CO take part.
$\sigma$-bond $\rightarrow$ Empty hybrid orbital of metal and filled molecular orbital of carbon mono oxide.
48. Acetic acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ is partially dimerised to $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)_{2}$ in the vapour phase. At a total pressure of 0.200 atm , acetic acid is $92.0 \%$ dimerized at 298 K .

The value of equilibrium constant of dimerisation under these conditions is
(A) 57.5
(B) 9.7
(C) 97
(D) 194

Ans. (D)
Sol. $2 \mathrm{CH}_{3} \mathrm{COOH} \longrightarrow\left(\mathrm{CH}_{3} \mathrm{COOH}\right)_{2}$
a
a-0.92a
0.08 a
0.46 a
0.46 a
$\mathrm{Kp}=\frac{\frac{0.46 \mathrm{a}}{0.54 \mathrm{a}} \times 0.02}{\left(\frac{0.08 \mathrm{a}}{0.54 \mathrm{a}} \times 0.02\right)^{2}} \simeq 194$.
49. Silanes are silicon hydrides of general formula $\mathrm{Si}_{n} \mathrm{H}_{2 n+2}$ and have several applications. From the data given below, the bond dissociation enthalpy of $\mathrm{Si}-\mathrm{Si}$ bond can be deduced as

$$
\begin{aligned}
& \Delta \mathrm{H} \text { of the reaction } 2 \mathrm{Si}(\mathrm{~s})+3 \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{Si}_{2} \mathrm{H}_{6}(\mathrm{~g}) \text { is } 80.3 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
& \text { Bond dissociation enthalpy for } \mathrm{H}-\mathrm{H}=436 \mathrm{~kJ} / \mathrm{mol} \\
& \text { Bond dissociation enthalpy for } \mathrm{Si}-\mathrm{H}=304 \mathrm{~kJ} / \mathrm{mol} \\
& \Delta \mathrm{f}_{\mathrm{H}}[\mathrm{Si}(\mathrm{~g})] 450 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

(A) $-304 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(B) $384.3 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(C) $304 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(D) $-384.3 \mathrm{~kJ} \mathrm{~mol}^{-1}$

Ans. BONUS
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Sol. $\quad 2 \mathrm{Si}_{(\mathrm{s})}+3 \mathrm{H}_{2} \longrightarrow \mathrm{Si}_{2} \mathrm{H}_{6} \quad \Delta \mathrm{H}=80.3 \mathrm{~kJ} / \mathrm{mole}$


$$
[(\mathrm{Si}-\mathrm{Si})+6(\mathrm{Si}-\mathrm{H})]
$$

$80.3=2 \times 405+3 \times 436-[(\mathrm{Si}-\mathrm{Si})+6(304)]$
$(\mathrm{Si}-\mathrm{Si})_{\text {Bond energy }}=304 \mathrm{~kJ} / \mathrm{mole}$
50. In the following reaction, three products $a, b, c$ are obtained.


The approximates experimental yields of the three compounds were $64 \%, 33 \%$ and $3 \%$.
Which of the following is the correct with respect to yield and the corresponding product ?
(A) (a)-33\% ; (b)-64\% ;
(c)-3\%
(B) (a)
(D) (a)-64\% ; (b)-3\% ;
(c) $33 \%$
(C) (a) $-3 \%$; (b) $-33 \%$; (c) $-64 \%$
c) $-33 \%$

Ans. (B)
Sol. \% yield $\propto$ stability of Alkene
Decreasing order of stability

(b)


51. Which of the following represents the correct order of dipole moment?
(A) $\mathrm{NH}_{3}>\mathrm{NF}_{3}>\mathrm{H}_{3} \mathrm{O}$
(B) $\mathrm{NH}_{3}>\mathrm{H}_{2} \mathrm{O}>\mathrm{NF}_{3}$
(C) $\mathrm{H}_{2} \mathrm{O}>\mathrm{NH}_{3}>\mathrm{NF}_{3}$
(D) $\mathrm{H}_{2} \mathrm{O}>\mathrm{NF}_{3}>\mathrm{NH}_{3}$

Ans. (C)
Sol.


Hence $\mathrm{H}_{2} \mathrm{O}>\mathrm{NH}_{3}>\mathrm{NF}_{3}$

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52．The best reaction sequence for the synthesis of 2－pentanone would be－
（A）

（B）

（C）

（D）


Ans．（B）

Sol．


53．Haemoglobin is a Fe containing protein responsible for oxygen transport in the blood．The curves given below indicate the percentage saturation of haemoglobin by $\mathrm{O}_{2}$ as a function of partial pressure of $\mathrm{O}_{2}$ ．


Which of the following statement／s is／are correct for the given curves？

I．In presence of $\mathrm{CO}_{2}$ ，higher $\mathrm{P}_{\mathrm{O}_{2}}$ is needed for a given percentage saturation

II．In presence of $\mathrm{CO}_{2}$ ，lower $\mathrm{P}_{\mathrm{O}_{2}}$ is needed for a given percentage saturation

III．The maximum percentage saturation is not affected by the presence of $\mathrm{CO}_{2}$

IV．In the absence of $\mathrm{CO}_{2}$ ，maximum saturation of haemoglobin occurs at lower $\mathrm{p}_{\mathrm{O}_{2}}$
（A）I and IV
（B）II and IV
（C）I，III and IV
（D）II and III

Ans．（C）
Sol．According to given information graph I would be in presence of $\mathrm{CO}_{2}$ and II would be in absence of $\mathrm{CO}_{2}$ ．
Now we can conclude from graph that
（i）In presence of $\mathrm{CO}_{2}$ higher $\mathrm{P}_{\mathrm{O}_{2}}$ in needed for a given percentage saturation．
（ii）The maximum percentage saturation is not affected by presence of $\mathrm{CO}_{2}$ ．
（ii）In the absence of $\mathrm{CO}_{2}$ ，maximum saturation of haemoglobin occurs at lower $\mathrm{P}_{\mathrm{O}_{2}}$ ．
54. An appropriate reagent for the conversion of 1-propanol to 1-propanal is
(A) acidified potassium dichromate
(B) alkaline potassium permanganate
(C) pyridinium chlorochromate
(D) acidified $\mathrm{CrO}_{3}$

Ans. (C)
Sol. Mild oxidising agent pyridinium chlorochromate (PCC) will oxidise primary alcohol into aldehyde.
55. A student performed an experiment to determine the molecular formula of a given sample of hydrated copper(II) sulphate by weighing the sample before and after heating. The formula obtained experimentally was $\mathrm{CuSO}_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}$ while the actual formula of the given sample is $\mathrm{CuSO}_{4}$. $5 \mathrm{H}_{2} \mathrm{O}$. Which experimental error would account for the wrongly obtained result ?
(A) During heating, some of the hydrated copper(II) sulphate was lost
(B) The hydrated sample was not heated long enough to remove all the water present
(C) Weight of the hydrated sample recorded was less than the actual weight taken
(D) The balance used in the study showed all weights consistently high by 0.10 g .

Ans. (A)
Sol. $\quad W_{i}=m($ ini $)=m\left(\mathrm{CuSO}_{4} \cdot x \mathrm{H}_{2} \mathrm{O}\right)$
$\mathrm{w}_{\mathrm{f}}=\mathrm{m}($ final $)=\mathrm{m}\left(\mathrm{CuSO}_{4}\right)$ *(possibly dehydrated)
$\mathrm{m}_{\text {water }}=\mathrm{W}_{\mathrm{i}}-\mathrm{W}_{\mathrm{f}}$
$n_{\text {water }}=\frac{W_{i}-W_{f}}{18}$
$\mathrm{n}_{\mathrm{CuSO}_{4}}=\frac{\mathrm{W}_{\mathrm{f}}}{\mathrm{M}_{\mathrm{CuSO}_{4}}}$
$x=\frac{\mathrm{n}_{\mathrm{w}}}{\mathrm{n}_{\mathrm{CuSO}_{4}}}=\frac{\mathrm{W}_{\mathrm{i}}-\mathrm{W}_{\mathrm{f}}}{18} \times \frac{\mathrm{M}_{\mathrm{CuSO}_{4}}}{\mathrm{~W}_{\mathrm{f}}}$
$x \propto\left(\frac{W_{i}}{W_{f}}-1\right)$
Correct value of $x$ is 5
Experimental value of $x$ is 5.5
Now, Option (A) is absurd, since $\mathrm{CuSO}_{4}$ cannot evaprate.
$(C)$ is wrong If $W_{i}$ is less than correct value $X_{\text {experi }}$ should be $<5$.
$X_{\exp }=\frac{W_{i}^{\text {correct }}+0.1}{W_{f}^{\text {correct }}+0.1}$
$\because \quad \frac{\mathrm{W}_{\mathrm{i}}^{\text {correct }}}{\mathrm{W}_{\mathrm{f}}^{\text {correct }}}>1 \quad$ ；adding same no to numerator \＆denominator will decrease the fraction．
Now，look at（B）

$$
\begin{aligned}
& \mathrm{W}_{\mathrm{i}}=\mathrm{m}\left(\mathrm{CuSO}_{4} \cdot \mathrm{xH}_{2} \mathrm{O}\right) \\
& \mathrm{W}_{\mathrm{f}}=\mathrm{m}\left(\mathrm{CuSO}_{4} \cdot \mathrm{yH}_{2} \mathrm{O}\right) ; y<x
\end{aligned}
$$

Mass of water evaporated $=W_{i}-W_{f}^{\prime}$
Moles of water evaporated $=\frac{\mathrm{W}_{\mathrm{i}}-\mathrm{W}_{\mathrm{f}}^{\prime}}{18}$

$$
\begin{aligned}
\mathrm{x} & =\frac{\mathrm{n}_{\mathrm{w}}}{\mathrm{n}_{\mathrm{CuSO}_{4}}}=\frac{\mathrm{M}_{\mathrm{CuSO}_{4}}}{18} \times \frac{\mathrm{W}_{\mathrm{i}}-\mathrm{W}_{f}^{\prime}}{\mathrm{W}_{f}^{\prime}} \longleftarrow \text { Since we (wrongly) believe it to be anhydrous. } \\
& \mathrm{x}
\end{aligned}
$$

If some water of crystallization is left， $\mathrm{W}_{\mathrm{f}}^{\prime}$ must be $<\mathrm{W}_{\mathrm{f}}$（the correct value）．
Thus，the incorrect value must be＜5．But it is claimed as 5．5．
Hence，none of the options（A），（B），（C）or（D）are correct．In true spirit of chemical science，this question is ought to be a bonus．However if we assume spillage／any other loss（A）may be taken as the answer．

56．Malic acid is a dicarboxylic acid present in apples and it has the following structure


Which of the following synthetic routes will give（ $\pm$ ）malic acid？
（i） HBr
（i）

（i） KOH （aq．）
（ii）

（i）Red $\mathrm{P} / \mathrm{I}_{2}$
（iii）

（i） $\mathrm{B}_{2} \mathrm{H}_{6} / \mathrm{H}_{2} \mathrm{O}_{2}$
（iv） $\mathrm{H}_{2} \mathrm{C}=\mathrm{CH}-\mathrm{COOH} \xrightarrow[\text {（iii）} \mathrm{HCN} / \mathrm{H}_{3} \mathrm{O}^{+}]{\text {（ii）}[\mathrm{O}]}$
（A）i an dii
（B）ii
（C）ii and iii
（D）i and iii

Ans．（B）
Sol．

57. Which of the following cannot act as an oxidising agent?
(A) $\mathrm{S}^{2-}$
(B) $\mathrm{Br}_{2}$
(C) $\mathrm{HSO}_{4}^{-}$
(D) $\mathrm{SO}_{3}^{2-}$

Ans. (A)
Sol. As sulphide $\left(\mathrm{S}^{2-}\right)$ is in its lowest oxidation state. Hence it cannot act as a oxidising agent.
58. Ellingham diagrams are plots of $\Delta \mathrm{G}^{\circ}$ vs temperature which have applications in metallurgy.
$2 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O} \quad \Delta \mathrm{G}(\mathrm{J})=-247500+55.85 \mathrm{~T} \quad \ldots \ldots \ldots \ldots \ldots \ldots .$. (I)
$2 \mathrm{CO}+\mathrm{O}_{2}=2 \mathrm{CO}_{2} \quad \Delta \mathrm{G}(\mathrm{J})=-282400+86.81 \mathrm{~T}$
The Ellingham diagrams for the oxidation of $\mathrm{H}_{2}(\mathrm{I})$ and $\mathrm{CO}(\mathrm{II})$ are given below.

The two lines intersect $\left(T_{E}\right)$ at 1125 K .


Which of the following is correct?
I. $\Delta G^{\circ}$ for reaction (i) is more negative at $T<1125 \mathrm{~K}$
II. $\Delta G^{0}$ for the reduction of $C O$ is more negative at $T<1125 \mathrm{~K}$
III. $\mathrm{H}_{2}$ is a better reducing agent at $\mathrm{T}>1125 \mathrm{~K}$
IV. $\mathrm{H}_{2}$ is a better reducing agent at $\mathrm{T}<1125 \mathrm{~K}$
(A) I and II
(B) I and III
(C) III only
(D) I and IV

Ans. (C)
Sol. According to the given data, Plot I is for CO as it has more negative $\Delta \mathrm{G}$ value Plot II is for $\mathrm{H}_{2}$. And as we know in the Ellingham diagram, compound for which, the Plot lies below acts as a better reducing agent. So, at $\mathrm{T}>1125 \mathrm{~K}, \mathrm{H}_{2}$ is a better reducing agent.
Note: The given graph in the question is not according to given data in the question.
59. Hydrazine used in rocket fuels can be obtained by the reaction of ammonia and hydrogen peroxide according to the following equations
$2 \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{I}) \longrightarrow \mathrm{N}_{2} \mathrm{H}_{4}(\mathrm{I})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})\left(\Delta \mathrm{H}^{\circ}\right.$ reaction $\left.=-241 \mathrm{~kJ} / \mathrm{mol}\right)$
If $\Delta \mathrm{H}^{\circ}$ (formation) of $\mathrm{NH}_{3}, \mathrm{H}_{2} \mathrm{O}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ are $-46.1,-187.8$ and $-285.8 \mathrm{~kJ} / \mathrm{mol}$ respectively, $\Delta \mathrm{H}^{\circ}$ for the decomposition of hydrazine into $\mathrm{N}_{2}$ and $\mathrm{H}_{2}$ is
(A) $50.6 \mathrm{~kJ} / \mathrm{mol}$
(B) $241 \mathrm{~kJ} / \mathrm{mol}$
(C) $-50.6 \mathrm{~kJ} / \mathrm{mol}$
(D) $120.5 \mathrm{~kJ} / \mathrm{mol}$

Ans. (C)
Sol. $\quad 2 \mathrm{NH}_{3(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}_{2(\ell)} \longrightarrow \mathrm{N}_{2} \mathrm{H}_{4(\ell)}+2 \mathrm{H}_{2} \mathrm{O}_{(\ell)}$

$$
\begin{aligned}
& \Delta_{\text {reaction }}^{\circ}=\left(\Delta \mathrm{H}_{\mathrm{fN}_{2} \mathrm{H}_{4}}^{\circ}+2 \mathrm{x} \Delta \mathrm{H}_{\mathrm{f}}^{\circ} \mathrm{H}_{2} \mathrm{O}\right)-\left(2 \mathrm{x} \Delta \mathrm{H}_{\mathrm{f}\left(\mathrm{NH}_{3}\right)}^{\circ}+\Delta_{\mathrm{f}\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)}^{\circ}\right) \\
& -241=\Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{N}_{2} \mathrm{H}_{2}\right)+2 \times(-285.8)-2 x(-46.1)+187.8 \\
& \Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{N}_{2} \mathrm{H}_{2}\right)=-241+2 \times 285.8-2 \times 46.1-187.8 \\
& \Rightarrow \quad \Delta \mathrm{H}_{\mathrm{f}\left(\mathrm{~N}_{2} \mathrm{H}_{2}\right)}^{\circ}=50.6 \mathrm{~kJ} / \mathrm{mol} .
\end{aligned}
$$

Therefore, for the decomposition of hydrazine into $\mathrm{N}_{2} \& \mathrm{H}_{2}$ is $-50.6 \mathrm{~kJ} / \mathrm{mol}$.
60. $\mathrm{Sn}^{2+}$ compounds like SnO and $\mathrm{SnCl}_{2}$ are well known reducing agents, while $\mathrm{PbO}_{2}$ acts as an oxidizing agent. Which of the following statements support these reactivities?
I. SnO is more stable than $\mathrm{SnO}_{2}$
II. $\mathrm{Sn}^{4+}$ is more stable than $\mathrm{Sn}^{2+}$
III. $\mathrm{Pb}^{4+}$ is more stable than $\mathrm{Pb}^{2+}$
IV. $\mathrm{Pb}^{2+}$ is more stable than $\mathrm{Pb}^{4+}$
(A) I and III
(B) I, III and IV
(C) II and IV
(D) I, II and IV

Ans. (C)
Sol. $\mathrm{SnO}_{\mathrm{H}}^{+2} \longrightarrow \mathrm{SnO}_{2}^{+4} \quad \stackrel{+4}{\mathrm{PbO}_{2}} \longrightarrow \stackrel{+2}{\mathrm{PbO}}$

$$
\stackrel{+2}{\mathrm{SnCl}_{2} \longrightarrow+4} \mathrm{SnCl}_{4}
$$

$\mathrm{Sn}^{+4}$ is more stable than $\mathrm{Sn}^{+2} \& \mathrm{~Pb}^{+2}$ is more stable than $\mathrm{Pb}^{+4}$.
So, $\mathrm{Sn}^{+2}$ acts as reducing agents \& $\mathrm{Pb}^{+4}$ acts as oxidising agents.
Above fact can also be explain by inert pair effect.
61. A fuel/ oxidant system consisting of N ,N-dimethylhydrazine $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{2}$ and $\mathrm{N}_{2} \mathrm{O}_{4}$ (both liquids) is used in space vehicle propulsion. The liquid components are mixed stichiometrically so that $\mathrm{N}_{2}$, $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ are the only products. If all gases are under the same reaction conditions, number of moles of gases produced from 1 mole of $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NNH}_{2}$ is
(A) 3
(B) 6
(C) 9
(D) 4.5

Ans. (C)
Sol. $\quad\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N} \mathrm{NH}_{2}+2 \mathrm{~N}_{2} \mathrm{O}_{4} \longrightarrow 3 \mathrm{~N}_{2}+2 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
One mole of $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{~N} \mathrm{NH}_{2}$ will produce $(3+2+4=9)$ moles of gases.
62. An ether $(X)$ with molecular formula $\mathrm{C}_{5} \mathrm{H}_{10} \mathrm{O}$ reacts with excess of hot aq. HI to give a product which on further reaction with hot NaOH in ethanol forms 1,3 pentadiene. Structure of X is
(A)

(B)

(C)

(D)


Ans. (B)

Sol.

63. Compound ' $Y$ ' with molecular formula $\mathrm{C}_{8} \mathrm{H}_{9} \mathrm{Br}$ gives a precipitate on heating with alcoholic $\mathrm{AgNO}_{3}$. Oxidation of ' $Y$ ' gives products ' $Z$ ' $\left(\mathrm{C}_{8} \mathrm{H}_{6} \mathrm{O}_{4}\right)$ which gives an anhydride upon heating.
Compound ' $Y$ ' is
(A)

(B)

(C)

(D)


Ans. (C)

Sol.



64. The observed effective magnetic moment of two octahedral complexes,
$\mathrm{K}_{4}\left[\mathrm{Mn}(\mathrm{CN})_{6}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{X})$ and $\mathrm{K}_{4}\left[\mathrm{Mn}(\mathrm{SCN})_{6}\right](\mathrm{Y})$ are 2.18 BM and 6.06 BM , respectively. Which of the following is correct?
I. $X$ is low spin complex with two unpaired electrons
II. $Y$ is high spin complex with 5 unpaired electrons
III. $X$ is a high spin complex with two unpaired electrons
IV. Y is a low spin complex with 5 unpaired electrons
(A) I and III
(B) I, II
(C) I, II and IV
(D) I, II and III

Ans. Bonus
Sol. $\mathrm{K}_{4}\left[\mathrm{Mn}(\mathrm{CN})_{6}\right] \cdot 3 \mathrm{H}_{2} \mathrm{O} \Rightarrow \mathrm{Mn}^{2+}$ with $\mathrm{CN}=6$ \& SFL
$\therefore$ Pairing will take place $\left(\mathrm{t}_{2 g}^{221} \mathrm{e}_{\mathrm{g}}^{00}\right)$
$\Rightarrow$ Low spin complex with one unpaired electron．
$\mathrm{K}_{4}\left[\mathrm{Mn}(\mathrm{SCN})_{6}\right] \Rightarrow \mathrm{Mn}^{2+}$ with $\mathrm{CN}=6 \& \mathrm{WFL}$
$\therefore$ Pairing will not take place $\left(\mathrm{t}_{2 \mathrm{~g}}^{111} \mathrm{e}_{\mathrm{g}}^{11}\right)$
$\Rightarrow$ High spin complex with five unpaired electrons．
So，only II statements is correct，which matches with none of given options．So，question should be BONUS．
However，from the available options，（B）seem best．

65．The increasing reactivity of the sites（a－d）in the following compound is $S_{N} 1$ reaction is

（A） d $>$ b $>$ c $>$ a
（B） d $>$ c $>$ a $>$ b
（C） d $>$ c $>$ b $>$ a
（D） c $>$ d $>$ b $>$ a

Ans．（C）
Sol．Rate of $S_{N} 1$ reaction $\propto$ Stability of carbocation Stability of carbocation





66．Which of the following has the shortest bond length ？
（A） $\mathrm{O}_{2}$
（B） $\mathrm{O}_{2}^{-}$
（C） $\mathrm{O}_{2}^{+}$
（D） $\mathrm{O}_{2}^{-2}$

Ans．（D）
Sol．$\quad \mathrm{O}_{2}{ }^{+}(\mathrm{BO}=2.5$ ；maximum in available options $)$
So，it will have shortest bond length．

67．Which of the following statement／s is／are correct about weak acids in aqueous solutions？
I．When $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$ of a monoprotic acid， $50 \%$ of the acid is ionised
II．If $\mathrm{pH}=\mathrm{pKa}_{2}$ of a diprotic acid，the average charge of all the ionised species is 0.5
III．When $\mathrm{pH}=\mathrm{pKa}+1,10 \%$ of the acid is ionised
IV．When $\mathrm{pH}=7,50 \%$ of a monibasic acid is ionised
（A）I and IV
（B）I，II and IV
（C）I，II and IV
（D）I only

Ans．（D）
Sol．When $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$ of a monoprotic acid，$[\mathrm{A}]_{\mathrm{eq}}=[\mathrm{HA}]_{\mathrm{eq}}$ ．
So， $50 \%$ of acid is ionised．
68. 'lodine number' is the grams of iodine atoms (atomic mass $=127 \mathrm{~g} \mathrm{~mol}^{-1}$ ) that can react completely with 100 g of a vegetable oil. lodine monochloride (ICI) is a reagent used to determine iodine number. In an experiment, $25.00 \mathrm{~cm}^{3}$ of $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{ICI}$ was added to 127 g of the oil. The unreacted ICI was found to be equivalent to $40.00 \mathrm{~cm}^{3}$ of $0.10 \mathrm{~mol} \mathrm{dm}^{-3}$ of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$.

The iodine number of the oil can be deduced as
(A) 127
(B) 100
(C) 200
(D) 50

Ans. Bonus
Sol. $\quad \mathrm{I}-\mathrm{Cl}$ used $=25 \mathrm{~mL} \times 0.1 \mathrm{M}=2.5 \mathrm{mmol}$
meq of I-Cl left $\quad=$ meq of hypo reacted

$$
\begin{aligned}
& =40 \mathrm{~mL} \times 0.1 \mathrm{~N} \\
& =4 \mathrm{meq}
\end{aligned}
$$

$\therefore \quad \mathrm{mmol}$ of $\mathrm{I}-\mathrm{Cl}$ left $=\frac{4}{2}=2 \mathrm{mmol}$
Thus, mmol of $\mathrm{I}-\mathrm{Cl}$ reacted with 127 g vegetable oil $=2.5-2=0.5 \mathrm{mmol}$
Thus, mmol of ICl with 100 g of oil $=0.5 \mathrm{mmol} \times \frac{100}{127}$
Now, each mol of I-Cl contains 127 g of lodine atoms.
Thus, mass of iodine atom that combines from $\mathrm{I}-\mathrm{Cl}$ on vegetable oil $=\frac{50}{127} \times 127 \mathrm{mg}=50 \mathrm{mg} .=$ 0.05 g

Note: (i) There seems to be an error in the printed paper.
$\mathrm{l}-\mathrm{Cl}$ will add across $\mathrm{C}=\mathrm{C}$ as follows :


As per the 'definition' offered in the paper, '50' may be the answer. However, going by the correct standard definition of iodine number : instead of 1 mol of $\mathrm{I}-\mathrm{CI}, 1 \mathrm{~mol}$ of $\mathrm{I}_{2}$ can be added. Thus, iodine number will be 100.
Final verdict: $\quad 68$ : Bonus
Assuming the error of $10^{3}$ is neglected,
(B) should be the answer (by standard definition).
(D) may be offered as answer, if the definition given in paper is taken as such.

## Comment:

It is a potentially good but improperly worded question.
69. When NiO is doped with a small quantity of $\mathrm{Li}_{2} \mathrm{O}$
(A) both cation and anion vacancies are generated
(B) Shottky defects are generated
(C) NiO becomes an n-type semiconductor
(D) NiO becomes a p-type semiconductor

Ans. (D)
Sol. When NiO is doped with a small quantity of $\mathrm{Li}_{2} \mathrm{O}$, a $\mathrm{Ni}^{2+}$ can be expected to be replaced by $2 \mathrm{Li}^{+}$. A decrease in unpaired electrons would make NiO a p-type semiconductor.
70. When a sample of gas kept at $20^{\circ} \mathrm{C}$ and 4.0 atm is heated to $40^{\circ} \mathrm{C}$ at constant volume
(A) average speed of the gas molecules will decrease.
(B) number of collisions between the gas molecules per second will remain the same.
(C) average kinetic energy of the gas will increase.
(D) pressure of the gas will become 8 atm.

Ans. (C)
Sol. $K E_{\text {avg. }}=\frac{f}{2} n R T$
As $\mathrm{T}_{\uparrow}, \mathrm{KE}_{\text {avg } . \uparrow}$
71. Addition of bromine to cis-3-hexene gives
(A) racemic dibromide
(B) a mixture of diastereomeric dibromides
(C) optically active dibromide
(D) meso dibromide

Ans. (A)

Sol.

72. An organic compound " X " forms an orange-yellow precipitate with 2,4 -DNP reagent. It does not react with aqueous $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right] \mathrm{NO}_{3}$. X on reduction with $\mathrm{NaBH}_{4}$ gives a secondary alcohol and on oxidation with nitric acid yields a dicarboxylic acid containing the same number of carbon atoms.
On bromination, $X$ gives a monobromo product. On the basis of these reactions, it can be concluded that X
I. contains aldehydic carbonyl group.
II. contains ketonic carbonyl group.
III. contains ester carbonyl group.
IV. does not contain $\mathrm{C}=\mathrm{C}$ bonds.
(A) I only
(B) III and IV
(C) III only
(D) II and IV

Ans. (D)
Sol. An organic compounds ' $X$ ' forms and orange yellow precipitate with 2, 4-DNP reagent but does not react with aqueous $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right] \mathrm{NO}_{3}$ confirms presence of $\overline{\mathrm{C}}=\mathrm{O}$ group in form of ketone.
' X ' on reduction with $\mathrm{NaBH}_{4}$ gives secondary alcohol again suggests presence of ketone.
' X ' on bromination gives mono bromo product which suggests absence of $>\mathrm{C}=\mathrm{C} \backslash$ bond because in presence of $\lambda \mathrm{C}=\mathrm{C}^{\prime} \backslash$ dibromo product would have been formed.

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73. The undissociated form of a weak organic acid HA can be extracted from the aqueous phase into an organic phase using a water-immiscible organic solvent according to the following scheme


Which of the following is/are correct for this extraction?
I. $[\mathrm{HA}]_{\text {org }} /[\mathrm{HA}]_{\mathrm{aq}}$ depends on the pH of the aqueous phase
II. HA can be efficiently extracted from basic aqueous solutions
III. $[\mathrm{HA}]_{\text {org }} /[\mathrm{HA}]_{\text {aq }}$ depends on the initial concentration of HA
IV. $[H A]_{\text {org }} /[H A]_{\mathrm{aq}}+[\mathrm{A}]$ depends on the pH of the aqueous phase
(A) II and IV
(B) IV only
(C) I only
(D) III and IV

Ans. (B)

Sol.


Even if HA reacts / dissociates in any medium ;

$$
\begin{equation*}
\frac{[\mathrm{HA}]_{\mathrm{ORG}}}{[\mathrm{HA}] \mathrm{aq}}=\mathrm{K}_{\mathrm{D}} \text { will be always a constant. } \tag{i}
\end{equation*}
$$

Thus, I and III are wrong.
Now, consider (II). Adding more base will pull the aqueous equilibrium towards right side. Thus, organic HA will be pulled towards aqueous phase. Hence, its extraction by organic phase will be hampered.

Thus (ii) is wrong.
Obviously, only (iv) remains as the correct option. Hence (B) is the answer.

## Comment :

$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]_{\mathrm{aq}}}$
$\frac{\mathrm{Ka}}{\left[\mathrm{H}^{+}\right]}=\frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]_{\mathrm{aq}}}$
$\therefore \quad \frac{\mathrm{K}_{\mathrm{a}}+\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}^{+}\right]}=\frac{\left[\mathrm{A}^{-}\right]+[\mathrm{HA}]_{\mathrm{aq}}}{[\mathrm{HA}]_{\mathrm{aq}}}$
Dividing (i) by (ii) :
$\frac{[\mathrm{HA}]_{\mathrm{ORG}}}{\left[\mathrm{A}^{-}\right]+[\mathrm{HA}]_{\mathrm{aq}}}=\frac{\mathrm{K}_{\mathrm{D}}\left[\mathrm{H}^{+}\right]}{\mathrm{K}_{\mathrm{a}}+\left[\mathrm{H}^{+}\right]}=$function of pH .
74. The correct order of reactivity in nucleophilic substitution reaction of the following compounds $a, b$, and c would be
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CONH}_{2}$
(a)

(b)

(c)
(A) a $>$ c $>$ b
(B) $a>b>c$
(C) c $>$ b $>$ a
(D) $c>a>b$

Ans. (C)
Sol. Correct order of reactivity in nucleophilic substitution at acid derivative depends on following factors.

1. $\delta+$ charge on $\lambda \mathrm{C}=\mathrm{O}$ carbon
2. Inversely related to hinderance.

3. The complex ion that does not have d electrons in the metal atom is
(A) $\left[\mathrm{MnO}_{4}\right]^{-}$
(B) $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$
(C) $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}$
(D) $\left.\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$

Ans. (A)
Sol. $\mathrm{MnO}_{4}^{-} \Rightarrow \mathrm{Mn}^{7+}(3 \mathrm{~d} 0)$
76. The order in which the compounds $\mathrm{a}, \mathrm{b}$ and c react with $\mathrm{CH}_{3}$ l would be

(a)

(b)

(c)
(A) $a>c>b$
(B) $b>c>a$
(C) c $>$ b $>$ a
(D) b $>$ a $>$ c

Ans. (B)
Sol. Order in which compounds $\mathrm{a}, \mathrm{b}, \mathrm{c}$ react with $\mathrm{CH}_{3}-\mathrm{l}$ would depend upon nucleophilicity.


No flipping
$>$


No flipping but -I of nitrogen
$>$
undergoes amine inversion (flipping) so hinderance increases nucleophilicity decreases.
77. An organic compound 'P' with molecular formula $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{2}$ on oxidation gives benzoic acid as one of the products. the possible structure/s of ' $P$ ' is/are

(I)

(II)

(III)

(IV)
(A) I and III
(B) II and IV
(C) I and II
(D) II only

Ans. (C)
Sol. Organic compound 'P' $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{2}$ degree of unsaturation 06 and on oxidation gives benzoic acid.
The possible structure/s of ' $P$ ' is/are.

(I)

(II)

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78. The energy of an electron in the ground state of H atom is -136 eV .

The negative sign indicates that
(A) electrons are negatively charged.
(B) H atom is more stable than a free electron.
(C) energy of the electron in the H atom is lower than that of a free electron.
(D) work must be done to make a H atom from a free electron and proton.

Ans. (C)
Sol. The negative sign in energy of an electron indicates that energy of the electron in the H -atom is lower than that of a free electron.
79. Radius of Ar atom is 145 pm . The percentage volume occupied by an Ar atom at STP is
(A) 0.03
(B) 3.0
(C) 0.30
(D) 0.06

Ans. (A)
Sol. $\begin{aligned} & \% \\ = & =\frac{\frac{4}{3} \times \frac{22}{7} \times\left(1.45 \times 10^{-8}\right)^{3} \times 6.022 \times 10^{23}}{22400} \times 100 \\ & =0.034 \\ & \approx 0.03\end{aligned}$
80. The reduction of $\mathrm{O}_{2}$ to $\mathrm{H}_{2} \mathrm{O}$ in acidic solution has a standard reduction potential of 1.23 V . If the pH of the acid solution is increased by one unit, half cell potential will

$$
\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{e}^{-} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

(A) decrease by 59 mV
(B) increase by 59 mv
(C) decrease by 236 mV
(D) increase by 236 mV

Ans. (A)
Sol. $E=E^{\circ}-\frac{0.059}{n} \log _{10} Q_{p c}\left(\right.$ at $\left.25^{\circ} \mathrm{C}\right)$
$E_{i}=1.23-\frac{0.059}{4} \log _{10} \frac{1}{\left(10^{-x}\right)^{4}}$
\&
$E_{f}=1.23-\frac{0.059}{4} \log _{10} \frac{1}{\left(10^{-x-1}\right)^{4}}$
$E_{f}-E_{i}=0.059 \log _{10}\left(\frac{10^{-x-1}}{\left(10^{-x}\right)}\right)=-0.059 \mathrm{~V}$
$\therefore \mathrm{E}$ decreases by 59 mV


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