JEE Adv. October 2021

Question Paper With Text Solution

03 October. | Paper-2

CHEMISTRY

MATRIX

JEE Main & Advanced | XI-XII Foundation| VI-X Pre-Foundation

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JEE ADV. OCTOBER 2021 | 03 OCTOBER PAPER-2

SECTION – A

- This section contains SIX (06) questions.
- Each question has FOUR options (A), (B), (C) and (D). ONE OR MORE THAN ONE of these four option(s) is (are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme:

  Full Marks : +4 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, 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 +2marks;

  choosing ONLY (B) and (D) will get +2 marks;

  choosing ONLY (A) will get +1 mark;

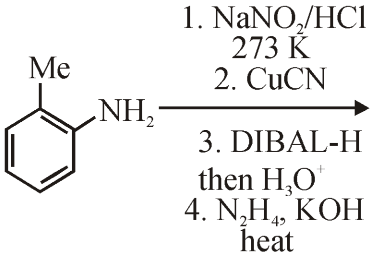
  choosing ONLY (B) will get +1 mark;

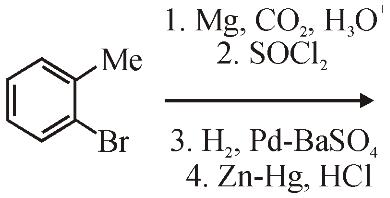
  choosing ONLY (D) will get +1 mark;

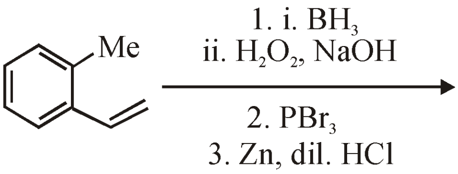
  choosing no option(s) (i.e. the question is unanswered) will get 0 marks and

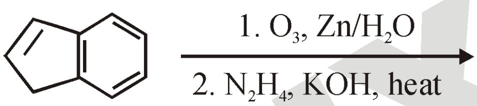
  choosing any other option(s) will get -2 marks.

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

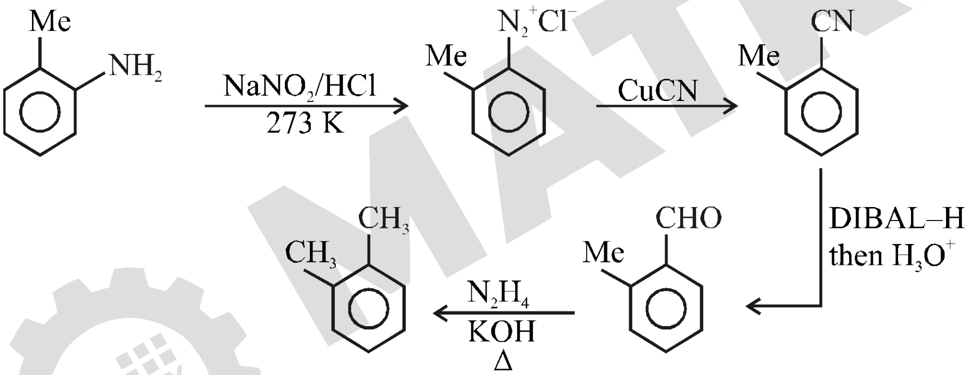
(A) 

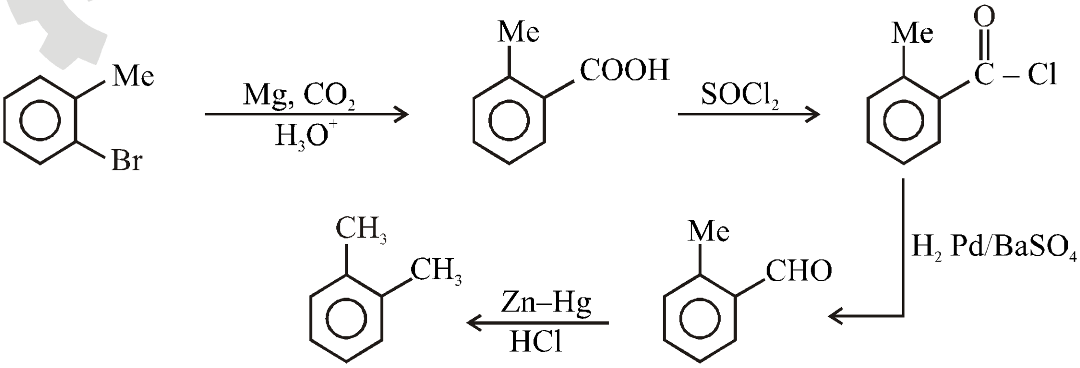
(B) 

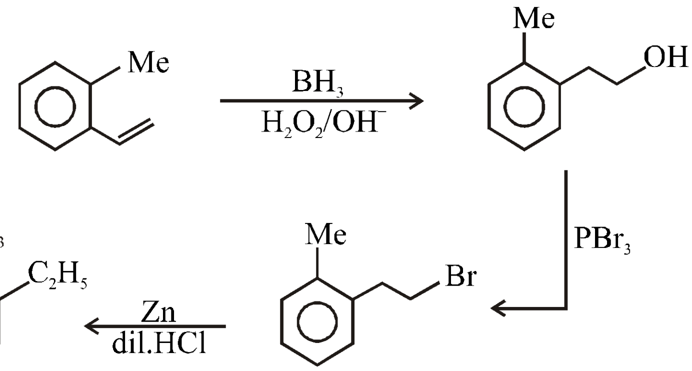
(C) 

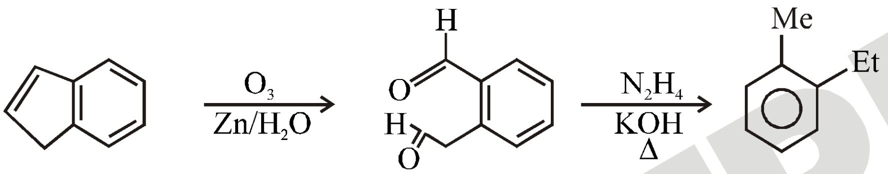
(D) 

Ans. (A), (B)

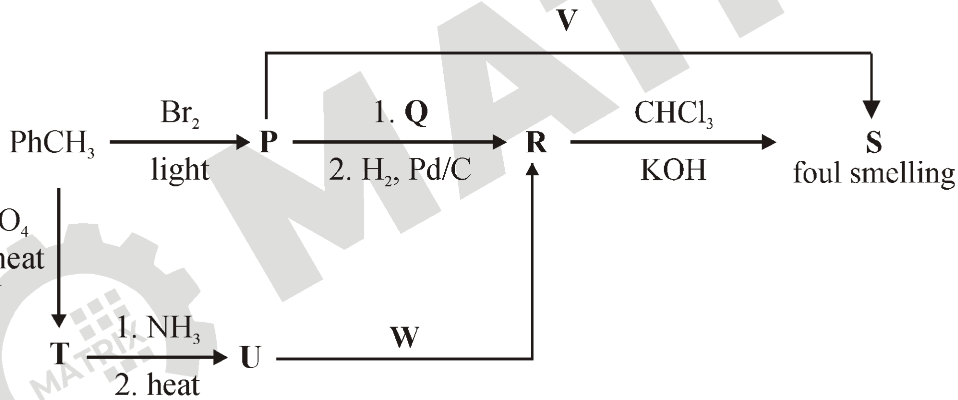
Sol. **(A)** 

(B) 

(C) 

(D) 

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



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

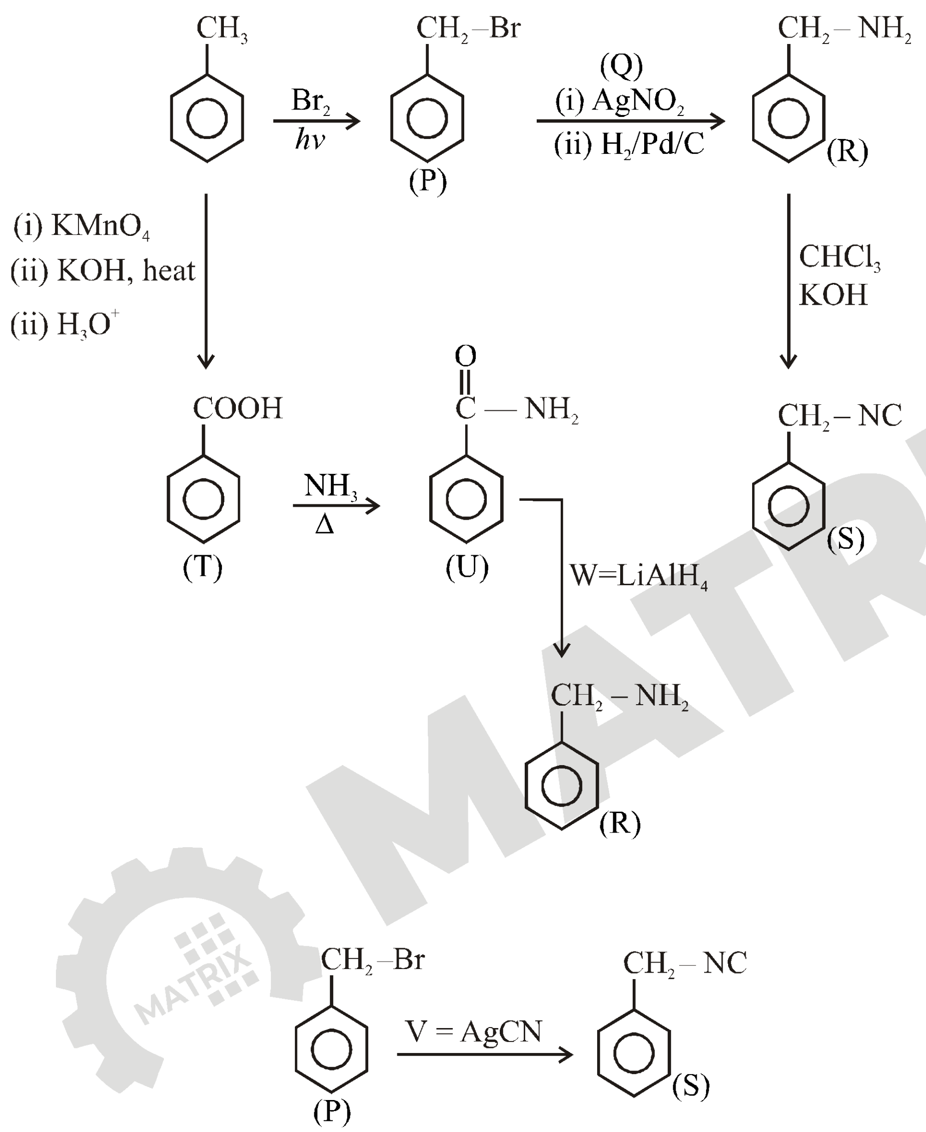
(B) **R** = benzenamine, **V** = KCN

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

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

Ans. (C), (D)

Sol.



3. For the following reaction

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

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

(Use: ln 2 = 0.693)

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

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

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

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

Ans. (B), (C), (D)

Sol.

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

	2	1	
After 50 sec	1	0.5	0.5

$$\frac{-d[X]}{2dt} = \frac{-d[Y]}{dt} = \frac{d[P]}{dt} = K[X]$$

Half life is 50 sec because concentration gets halved
Since overall order is 1

$$T_{\frac{1}{2}} = \frac{0.693}{k_x}$$

$$k_x = \frac{0.693}{50} sec^{-1}$$

for x $\quad k_x = 2k$

$$k = \frac{k_x}{2}$$

$$\frac{-d[X]}{dt} = 2\ k(x)^1$$

$$= \frac{2 \times 0.693}{50 \times 2} \times 1 = 13.86 \times 10^{-3}$$

at 100 sec

$[X] = 0.5$

$$-\frac{d[Y]}{dt} = K[X]^1$$

$$= \frac{0.693}{50 \times 2} \times 0.5 = 3.46 \times 10^{-3}$$

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

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

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

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

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

Ans. (A), (B), (C)

Sol. For a spontaneous reaction in an electrochemical cell

$$X_{(S)} \longrightarrow X^{2+}_{(aq)} + 2e^-$$

$$Y^{2+}_{(aq)} + 2e^- \longrightarrow Y_{(S)}$$

$$E_{Cell} = E^o_{Cell} \frac{-0.06}{2} \log \frac{[X^{2+}]}{[Y^{2+}]}$$

$$= E^o_{Cell} \frac{-0.06}{2} \log \frac{0.001}{0.1}$$

$$= E^o_{Cell} + 0.06$$

$E_{Cell} = +ve$

$E°_{Cell} = E^o_{Ni^{2+}/Ni} - E^o_{Cd^{2+}/Cd}$

$= – 0.24 – (0.4) = 0.16V$

$E_{cell} = E°_{Cell} + 0.06 = 0.22V$

Likewise

Cd/Fe and Ni/Pb also form such Cell.

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

(Note: py = pyridine

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

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

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

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

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

Ans. (A), (B), (D)

Sol. (A) $[FeCl_4]^- \rightarrow$ Tetrahedral

$[Fe(CO)_4]^{2-} \rightarrow$ Tetrahedral

(B) $[Co(CO)_4]^- \rightarrow$ Tetrahedral

$[CoCl_4]^{2-} \rightarrow$ Tetrahedral

(C) $[Ni(CO)_4] \rightarrow$ Tetrahedral

$[Ni(CN)_4]^{2-} \rightarrow$ square planar

(D) $[Cu(py)_4]^+ \rightarrow$ Tetrahedral

$[Cu(CN)_4]^{3-} \rightarrow$ Tetrahedral

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

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

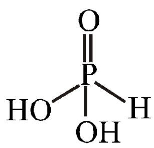
(B) While H_3PO_3 can act as reducing agent, H_3PO_4 cannot.

(C) H_3PO_3 is a monobasic acid.

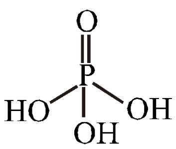
(D) The H atom of P–H bond in H_3PO_3 is not ionizable in water.

Ans. (A), (B), (D)

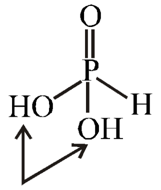
Sol. (A) $H_3PO_3 \xrightarrow[\text{Disprop}^n]{\Delta} H_3PO_4 + PH_3$

(B) 

← Reducing Hydrogen

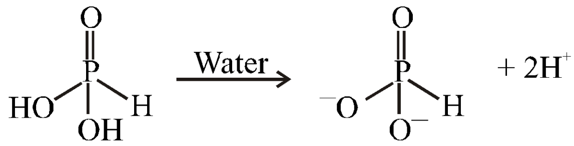


* Due to having reducing hydrogen H_3PO_3 can act as reducing agent.

(C) 

Acidic hydrogen

* H_3PO_3 is a dibasic acid.

(D) 

Phosphite ion

SECTION B

- This section contains **THREE (03**) question stems.
- There are **TWO (02)** questions corresponding to each question stem.
- The answer to each question is a **NUMERICAL VALUE.**
- For each question, enter the correct numerical value corresponding to the answer in the designated place using the mouse and the on-screen virtual numeric keypad.
- If the numerical value has more than two decimal places, truncate/round-off the value to TWO decimal places.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +2 If ONLY the correct numerical value is entered at the designated place;
  Zero Marks : 0 In all other cases.

Question Stem for Question Nos. 7 and 8

Question Stem

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

7. The value of α is ___.

Ans. 0.21 or 0.22

8. The value of **y** is ___.

Ans. 0.86

Sol. $\alpha = \frac{\wedge_m}{\wedge_m^o} = \frac{y \times 10^2}{4 \times 10^2} = \frac{y}{4}$

α' = degree of dissociation after dilution

$C' = \frac{C}{20}$ = new concentration.

$$HA \rightleftharpoons H^+ + A^-$$

C

$C - C\alpha \qquad C\alpha \qquad C\alpha$

K_a at C = K_a at C'

$$\frac{C\alpha^2}{1-\alpha} = \frac{C'(\alpha')^2}{1-\alpha'}$$

$$\frac{\left(\frac{y}{4}\right)^2}{1-\frac{y}{4}} = \frac{\frac{1}{20}\left(\frac{3y}{4}\right)^2}{1-\frac{3y}{4}}$$

$$\frac{4-3y}{4-y} = \frac{9}{20}$$

$80 - 60y = 36 - 9y$

$y = 0.86$

$y = \frac{y}{4}$

$\alpha = \frac{0.86}{4}$

$= 0.215$

Question Stem for Question Nos. 9 and 10

Question Stem

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

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

9. The value of **x** is ___.

Ans. 3.57

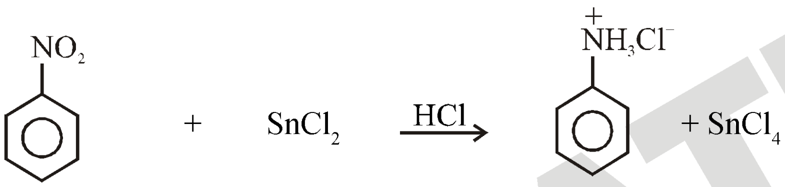
10. The value of **y** is ___.

Ans. 1.23

Sol. $Sn + HCl \longrightarrow SnCl_2$
xg

moles = $\frac{x}{119}$

moles of $SnCl_2$ formed = $\frac{x}{119}$ moles.



Valency factor = 6 Valency factor = 2 Valency factor = 6

equivalent of $SnCl_2$ = equivalent of salt formed

$\Rightarrow \frac{x}{119} \times 2 = \frac{1.29}{129} \times 6$

x = 3.57

equivalent of nitrobenzene = equivalent of $SnCl_2$

$\frac{y}{123} \times 6 = \frac{3.57}{119} \times 2$

y = 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 M $KMnO_4$ solution to reach the end point. Number of moles of Fe^{2+} present in 250 mL solution is $\mathbf{x} \times 10^{-2}$ (consider complete dissolution of $FeCl_2$). The amount of iron present in the sample is **y**% by weight.

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

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

11. The value of **x** is ___.

Ans. 1.87 or 1.88

12. The value of **y** is ___.

Ans. 18.75

Sol. % purity of iron sample = y%

mass of in sample = $5.6\times\frac{y}{100}$ g

$$Fe + HCl \longrightarrow FeCl_2$$

moles = $\frac{5.6y}{100\times 56}$

Molarity of $FeCl_2$ solution = $\frac{\frac{5.6y}{100\times 56}}{250}\times 1000$

Titration between $FeCl_2$ and $KMnO_4$,

$$\overset{+7}{KMnO_4} + \overset{+2}{FeCl_2} \longrightarrow \overset{2+}{Mn} + \overset{3+}{Fe}$$

Valency factor 5 1

at equivalence point,

equivalent of $KMnO_4$ = equivalent of $FeCl_2$

$$\Rightarrow 0.03\times\frac{12.5}{1000}\times 5 = \frac{5.6y}{100\times 56}\times\frac{25}{250}\times 1$$

y = 18.75

$x\times 10^{-2}$ = moles of Fe^{2+} in 250 ml solution

= moles of $FeCl_2$

$$= \frac{5.6\times 18.75}{100\times 56} = 0.01875 \Rightarrow x = 1.875$$

SECTION - C

- This section contains **TWO (02) paragraphs**. Based on each paragraph, there are **TWO (02)** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +3 If ONLY the correct option is chosen;

Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered);

Negative Marks : -1 In all other cases.

Paragraph

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

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

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

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

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

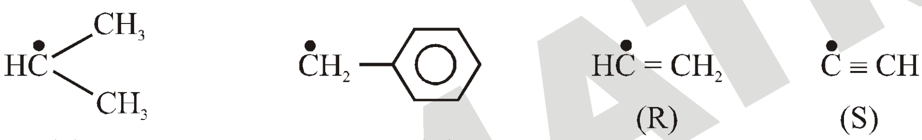
13. Correct match of the **C–H** bonds (shown in bold) in Column **J** with their BDE in Column **K** is

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

(A) P – iii, Q – iv, R – ii, S – i
(B) P – i, Q – ii, R – iii, S – iv
(C) P – iii, Q – ii, R – i, S – iv
(D) P – ii, Q – i, R – iv, S – iii

Ans. (A)

Sol. Greater the stability of radical formed, easier will be to break C – H bond.



(P) (Q) (R) (S)

Stability order ⇒

Q	>	P	>	R	>	S
↓		↓		↓		↓
88		95		110		132
(iv)		(iii)		(ii)		(i)

Option (A)

14. For the following reaction

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

the correct statement is

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

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

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

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

Ans. (D)

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

ΔH_{rxn} = BDE (C – H) + BDE (Cl – Cl) – BDE (C – Cl) – BDE (H – Cl)

= 105 + 58 – 85 – 103 = – 25 kcal/mol

Initiation Step :

$Cl - Cl \longrightarrow 2\dot{C}l$

$\Delta H°$ = BDE (Cl – Cl)

= 58 kcal/mol

Propagation Step :

$CH_4 + \dot{C}l \longrightarrow \dot{C}H_3 + HCl$

$\Delta H°$ = – BDE (H – Cl) + BDE (C – H)

= – 103 + 105

= 2 kcal/mol

$\dot{C}H_3 + Cl - Cl \longrightarrow CH_3Cl + \dot{C}l$

$\Delta H°$ = BDE (Cl – Cl) – B.D.E. (C – Cl)

= 58 – 85

= – 27 kcal/mol

Paragraph

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

15. Precipitate X is

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

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

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

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

Ans. (C)

Sol. $K_4[Fe(CN)_6] + FeSO_4 \rightarrow$

$K_2Fe[Fe(CN)_6]\downarrow + K_2SO_4$

White PPT

(×)

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

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

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

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

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

Ans. (D)

Sol. $FeSO_4 + NaNO_3 + \text{Conc. } H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NO + Na^+ + H_2O$

$NO + Fe^{+2}(aq) \rightarrow [Fe(NO)(H_2O)_5]^{+2}$

Brown ring complex

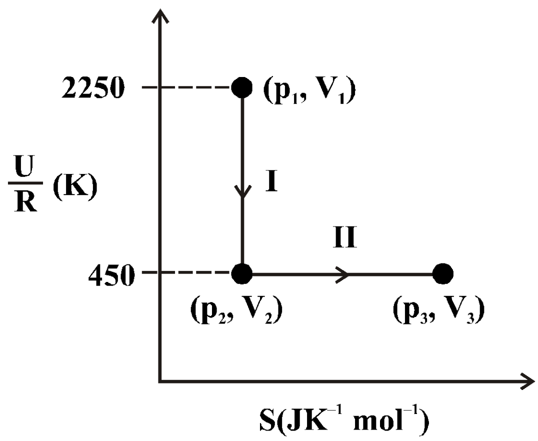
SECTION – D

- This section contains **THREE (03)** questions.
- The answer to each question is a **NON-NEGATIVE INTEGER**.
- For each question, enter the correct integer corresponding to the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If ONLY the correct integer is entered;

Zero Marks : 0 In all other cases.

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



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

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

Ans. 10

Sol. Process I $\rightarrow$ adiabatic reversible

Work done $= \Delta U$

(W_I) $= U_2 - U_1$

$= 450\ R - 2250\ R = -1800\ R$

also, $U_2 - U_1 = -1800\ R$

$\Rightarrow C_{v,m}(T_2 - T_1) = -1800\ R$

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

$T_2 = -\frac{1800 \times 2}{5} + 900$

$T_2 = 180\ K$

Process II $\rightarrow$ Isothermal reversible process

Work done $= -nRT_2 \ln\frac{V_3}{V_2}$

(W_{II})

$\Rightarrow W_{II} = W_I = -1 \times R \times T_2 \times \ln\frac{V_3}{V_2}$

$\Rightarrow -1800\ R = -R \times 180 \times \ln\frac{V_3}{V_2}$

$\Rightarrow \ln\frac{V_3}{V_2} = 10$

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

(Assume: Momentum is conserved when photon is absorbed.

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

Ans. 30

Sol. Change in velocity $(\Delta V) = \frac{h}{m.\lambda}$

$$= \frac{6.6\times10^{-34}\,\text{Js}}{\left(\frac{4\times10^{-3}\,\text{kg / mole}}{6\times10^{23}\,/\,\text{mol}}\right)\times330\times10^{-9}\,\text{m}}$$

$\Delta V = 0.3$ m/sec $= 30\frac{\text{cm}}{\text{sec}}$

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

Ans. 6.00

Sol. $ClO_2 + O_3 \longrightarrow \overset{+6}{Cl}O_3 + O_2 \longrightarrow$ average oxidation state of Cl = (+6)