

SECTION - 1

- This section contains **EIGHT (08)** questions.
- Each question has **FOUR** options (A), (B), (C) & (D). **ONE OR MORE THAN ONE** of these four option(s) is(are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If only (all) the correct option(s) is(are) chosen;

Partial Marks : +3 If all the four options are correct but ONLY three options are chosen;

Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, and both of which are correct;

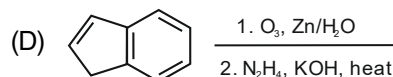
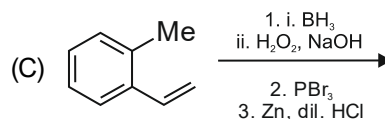
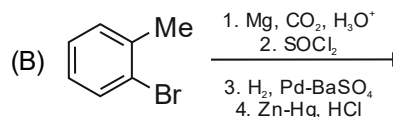
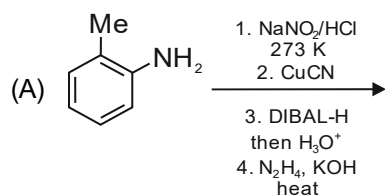
Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option;

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

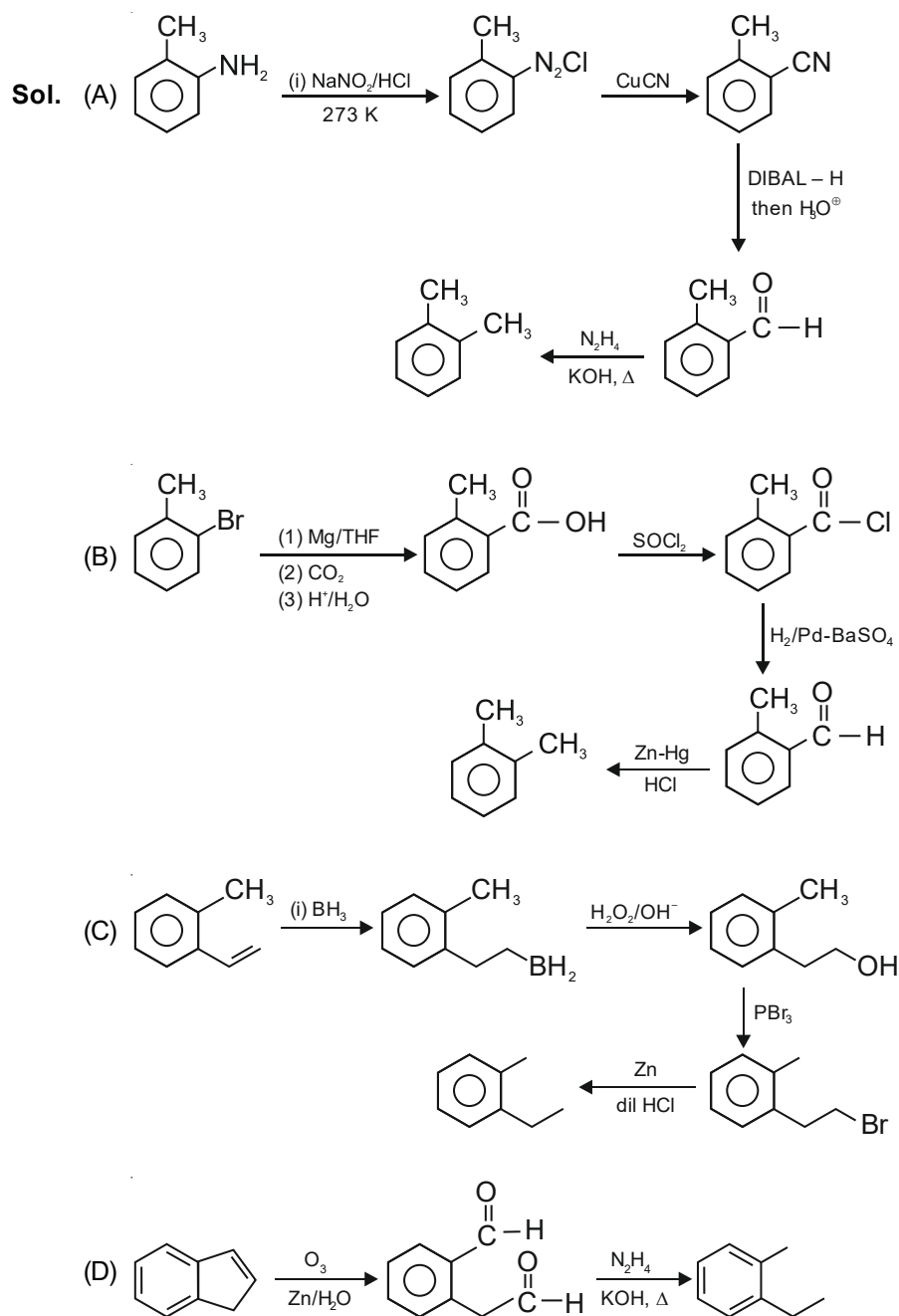
Negative Marks : -2 In all other cases.

- For example : in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answers, then choosing ONLY (A), (B) and (D) will get +4 marks;
choosing ONLY (A) and (B) will get +2 marks;
choosing ONLY (A) and (D) will get +2 marks;
choosing ONLY (B) and (D) will get +2 marks;
choosing ONLY (A) will get +1 mark;
choosing ONLY (B) will get +1 mark;
choosing ONLY (D) will get +1 mark;
choosing no option (i.e., the question is unanswered) will get 0 marks; and
choosing any other combination of options will get -2 mark.

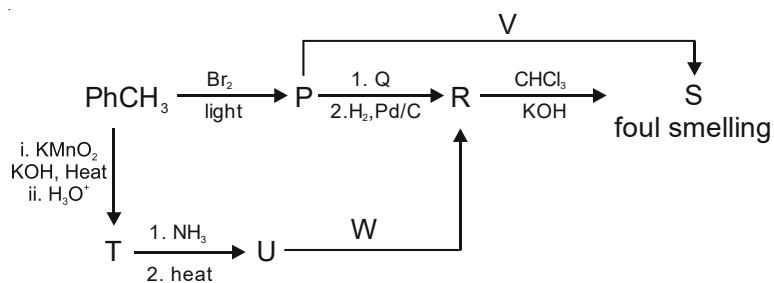
1. The reaction sequence(s) that would lead to *o*-xylene as the major product is(are)



Answer (A, B)



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



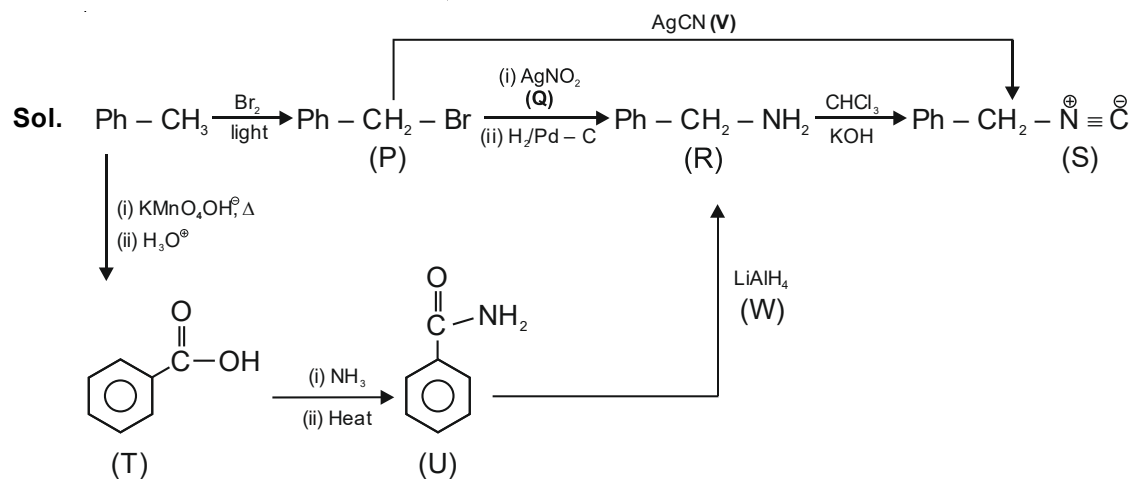
(A) $Q = \text{KNO}_2$, $W = \text{LiAlH}_4$

(B) $R = \text{benzenamine}$, $V = \text{KCN}$

(C) $Q = \text{AgNO}_2$, $R = \text{phenylmethanamine}$

(D) $W = \text{LiAlH}_4$, $V = \text{AgCN}$

Answer (C, D)

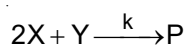


∴ Correct option are

Q = AgNO₂, R = phenylmethanamine

W = LiAlH₄, V = AgCN

3. For the following reaction



the rate of reaction is $\frac{d[\text{P}]}{dt} = k[\text{X}]$. 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 $13.86 \times 10^{-4} \text{ s}^{-1}$.

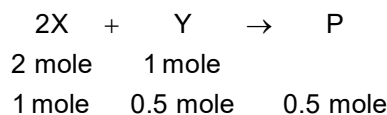
(B) Half-life of X is 50 s.

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

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

Answer (B,C,D)

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



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

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

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

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

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

At 50 sec

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

At 100 sec

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

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

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

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

$$\text{Pb}^{2+}/\text{Pb} \quad -0.13 \text{ V}$$

$$\text{Ni}^{2+}/\text{Ni} \quad -0.24 \text{ V}$$

$$\text{Cd}^{2+}/\text{Cd} \quad -0.40 \text{ V}$$

$$\text{Fe}^{2+}/\text{Fe} \quad -0.44 \text{ V}$$

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

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

(A) Cd and Ni

(B) Cd and Fe

(C) Ni and Pb

(D) Ni and Fe

Answer (A,B,C)

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

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

$$E = E^\circ + 0.06$$

$$(A) E^\circ = -(-.4) + (-.24) = .16 > 0$$

$$(B) E^\circ = -(-.4) + (-.44) = -.04 < 0 \text{ and } E_{\text{cell}} = -.04 + 0.06 = +0.02 > 0$$

$$(C) E^\circ = -(-.24) + (-.13) = .11 > 0$$

$$(D) E^\circ = -(-.24) + (-.44) = -.2 < 0$$

$$\therefore E_{\text{cell}} = -.2 + 0.06 = -.14 < 0$$

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

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

(Note: py = pyridine)

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

- (A) $[\text{FeCl}_4]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$
 (B) $[\text{Co}(\text{CO})_4]^-$ and $[\text{CoCl}_4]^{2-}$
 (C) $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$
 (D) $[\text{Cu}(\text{py})_4]^+$ and $[\text{Cu}(\text{CN})_4]^{3-}$

Answer (A,B,D)

Sol. $[\text{FeCl}_4]^- \rightarrow \text{Fe}^{3+}, 3d^5$ (weak field ligand) $\rightarrow sp^3$

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

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

$[\text{CoCl}_4]^{2-} \rightarrow \text{Co}^{2+}, 3d^7$ (weak field ligand) $\rightarrow sp^3$

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

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

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

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

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

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

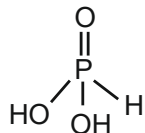
- (A) Upon heating, H_3PO_3 undergoes disproportionation reaction to produce H_3PO_4 and PH_3 .
 (B) While H_3PO_3 can act as reducing agent, H_3PO_4 cannot.
 (C) H_3PO_3 is a monobasic acid.
 (D) The H atom of P-H bond in H_3PO_3 is not ionizable in water.

Answer (A,B,D)

Sol. $4\text{H}_3\text{PO}_3 \xrightarrow{\Delta} \text{PH}_3 + 3\text{H}_3\text{PO}_4$

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

Structure of H_3PO_3 ,



It is a dibasic acid.

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

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

SECTION - 2

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

Full Marks : +2 If ONLY the correct numerical value is entered at the designated place.

Zero Marks : 0 In all other cases.

Question Stem for Question Nos. 7 and 8

Question Stem

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

7. The value of α is _____.

Answer (0.215)

8. The value of y is _____.

Answer (0.86)

Sol. Solution of Question Nos. 7 and 8

Molar conductivity of HX at infinite dilution

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

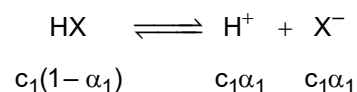
Molar conductivity of HX at conc. $c_1 = y \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$

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

On 20 times dilution of the solution of HX

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

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



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

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

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

$$y = 4\alpha_1 = 0.86$$

Question Stem for Question Nos. 9 and 10

Question Stem

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

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

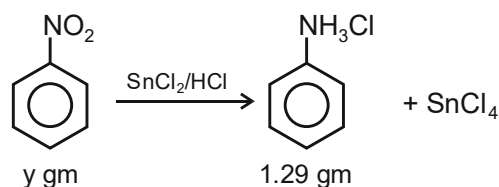
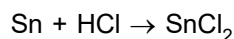
9. The value of x is _____.

Answer (3.57)

10. The value of y is _____.

Answer (1.23)

Sol. Solution of Question Nos. 9 and 10



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

$$\Rightarrow \text{Moles of nitrobenzene} = 0.01$$

$$\begin{aligned} \Rightarrow y &= 0.01 \times \text{Molar mass of nitrobenzene} \\ &= 0.01 \times 123 \\ y &= 1.23 \end{aligned}$$

Also

No. of eq. of nitrobenzene = No. of eq. of SnCl₂

$$6 \times (0.01) = 2 \times n_{\text{SnCl}_2}$$

$$n_{\text{SnCl}_2} = 0.03$$

$$\Rightarrow n_{\text{Sn}} = 0.03$$

$$w_{\text{Sn}} = 0.03 \times 119$$

$$x = 3.57$$

Question Stem for Question Nos. 11 and 12

Question Stem

A sample (5.6 g) containing iron is completely dissolved in cold dilute HCl to prepare a 250 mL of solution. Titration of 25.0 mL of this solution requires 12.5 mL of 0.03 M KMnO_4 solution to reach the end point. Number of moles of Fe^{2+} present in 250 mL solution is $x \times 10^{-2}$ (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)

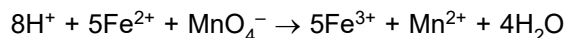
Use: Molar mass of iron as 56 g mol^{-1})

11. The value of x is _____.

Answer (1.875)

12. The value of y is _____.

Answer (18.75)

Sol. Solution of Question Nos. 11 and 12

For 25 ml,

$$\begin{aligned} \text{meq of Fe}^{2+} &= \text{meq of MnO}_4^- \\ &= 12.5 \times 0.03 \times 5 \end{aligned}$$

For 250 ml,

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

$$\begin{aligned} \text{moles of Fe}^{2+} &= \frac{18.75}{1000} \text{ mol} \\ &= 18.75 \times 10^{-3} \text{ mol} \\ &= 1.875 \times 10^{-2} \text{ mol} \end{aligned}$$

$$x = 1.875$$

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

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

$$y = 18.75\%$$

SECTION - 3

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

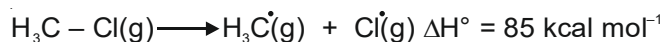
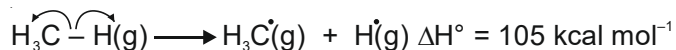
Full Marks : +3 If ONLY the correct option is chosen;

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

Negative Marks : -1 In all other cases.

Paragraph

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

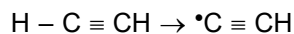
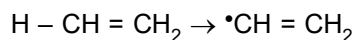
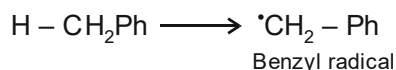
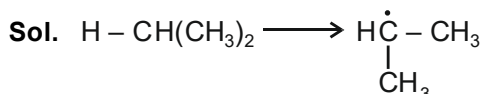


13. Correct match of the **C-H** bonds (shown in bold) in Column **J** with their BDE in Column **K** is

Column J	Column K
Molecule	BDE (kcal mol ⁻¹)
(P) H-CH (CH ₃) ₂	(i) 132
(Q) H-CH₂ Ph	(ii) 110
(R) H-CH=CH₂	(iii) 95
(S) H-C≡CH	(iv) 88

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

Answer (A)



Order of stability of free radical

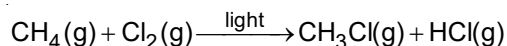
$$Q > P > R > S$$

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

∴ Order of bond energy :

$$S > R > P > Q$$

14. For the following reaction

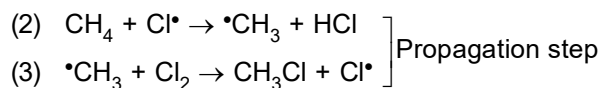


the correct statement is

- (A) Initiation step is exothermic with $\Delta H^\circ = -58 \text{ kcal mol}^{-1}$
 (B) Propagation step involving $\cdot\text{CH}_3$ formation is exothermic with $\Delta H^\circ = -2 \text{ kcal mol}^{-1}$
 (C) Propagation step involving CH_3Cl formation is endothermic with $\Delta H^\circ = +27 \text{ kcal mol}^{-1}$
 (D) The reaction is exothermic with $\Delta H^\circ = -25 \text{ kcal mol}^{-1}$

Answer (D)

Sol. (1) $\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$ (Initiation step) $\Delta H = 58 \text{ kcal/mol}$



Step (1) $\rightarrow$ Endothermic (bond breaking)

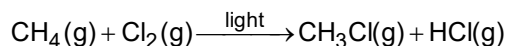
Step (2) $\rightarrow \Delta H = 105 - 103$

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

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

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

For complete reaction



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

$= -25 \text{ kcal/mol}$

Paragraph

The reaction of $\text{K}_3[\text{Fe}(\text{CN})_6]$ with freshly prepared FeSO_4 solution produces a dark blue precipitate called Turnbull's blue. Reaction of $\text{K}_4[\text{Fe}(\text{CN})_6]$ 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

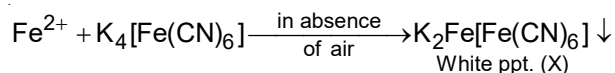
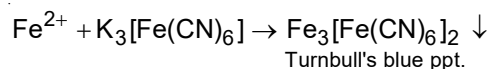
- (A) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (B) $\text{Fe}[\text{Fe}(\text{CN})_6]$
 (C) $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ (D) $\text{KFe}[\text{Fe}(\text{CN})_6]$

Answer (C)

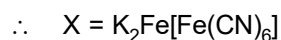
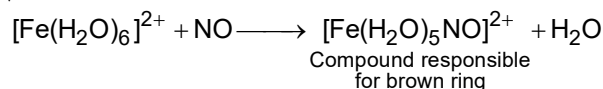
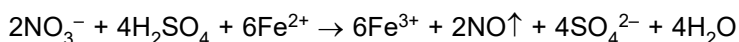
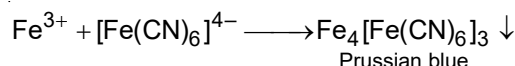
16. Among the following, the brown ring is due to the formation of

- (A) $[\text{Fe}(\text{NO})_2(\text{SO}_4)_2]^{2-}$
 (B) $[\text{Fe}(\text{NO})_2(\text{H}_2\text{O})_4]^{3+}$
 (C) $[\text{Fe}(\text{NO})_4(\text{SO}_4)_2]$
 (D) $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$

Answer (D)

Sol. Solution of Question Nos. 15 and 16

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



Brown ring is due to $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$

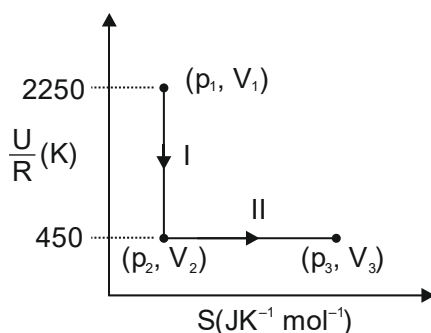
SECTION - 4

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

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

Zero Marks : 0 In all other cases.

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



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

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

Answer (10)

Sol. Process I is adiabatic reversible

Process II is reversible isothermal process

Process I - (Adiabatic Reversible)

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

$$\Delta U = -1800R$$

$$W_I = \Delta U = -1800R$$

Process II - (Reversible Isothermal Process)

$$T_1 = 900 \text{ K}$$

Calculation of T_2 after reversible adiabatic process

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

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

$$T_2 = 180 \text{ K}$$

$$W_{II} = -nRT_2 \ln \frac{V_3}{V_2} = W_I$$

$$\Rightarrow -1 \times R \times 180 \ln \frac{V_3}{V_2} = -1800R$$

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

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

(Assume: Momentum is conserved when photon is absorbed.)

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

Answer (30)

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

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

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

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

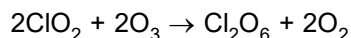
$$\Delta v = \frac{6 \times 6.6 \times 10^2}{33 \times 4} = 30 \text{ cm s}^{-1}$$

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

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

Answer (6)

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



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