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;

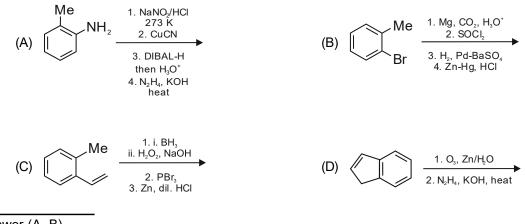
choosing ONLY (B) will get +1 mark;

choosing ONLY (D) will get +1 mark;

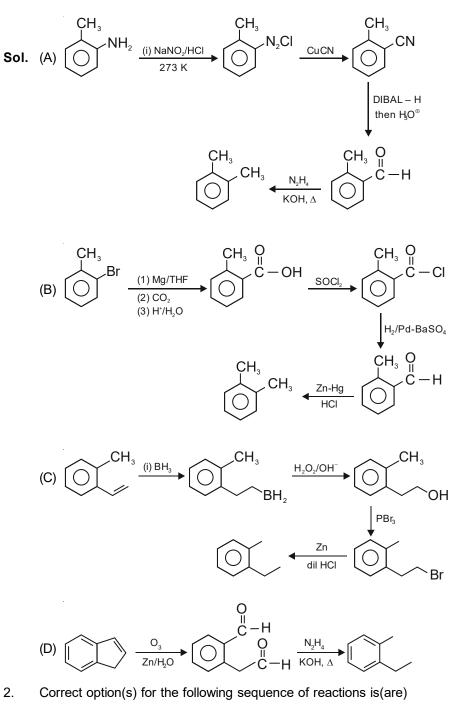
choosing no option (i.e., the question is unanswered) will get 0 marks; and

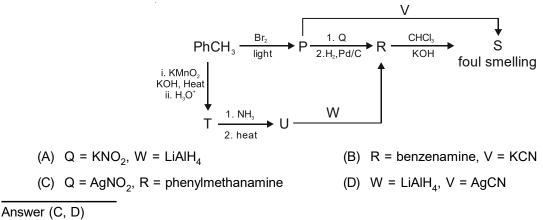
choosing any other combination of options will get -2 mark.

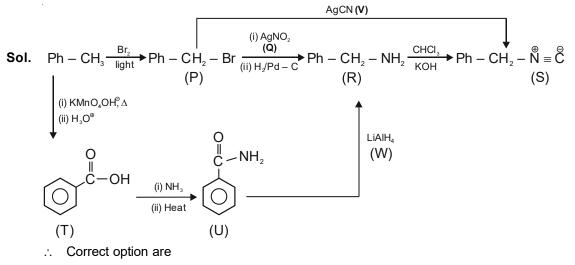
1. The reaction sequence(s) that would lead to *o*-xylene as the major product is(are)



Answer (A, B)







 $Q = AgNO_2$, R = phenylmethanamine

3. For the following reaction

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

the rate of reaction is $\frac{d[P]}{dt} = k[X]$. 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: In 2 = 0.693)

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

 $= k_1$

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

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

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

Answer (B,C,D)

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

$$2X + Y \rightarrow P$$
2 mole 1 mole
1 mole 0.5 mole 0.5 mole

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

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

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

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

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

At 50 sec

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

At 100 sec

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

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

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 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 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 |
|---------------|---------------|
|---------------|---------------|

Answer (A,B,C)

Sol. $X + Y^{2+} \to X^{2+} + Y$

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

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

(A) $E^{\circ} = -(-.4) + (-.24) = .16 > 0$
(B) $E^{\circ} = -(-.4) + (-.44) = -.04 < 0$ and $E_{cell} = -0.04 + 0.06 = +0.02 > 0$
(C) $E^{\circ} = -(-.24) + (-.13) = .11 > 0$
(D) $E^{\circ} = -(-.24) + (-.44) = -.2 < 0$

 \therefore E_{cell} = -0.2 + 0.06 = -0.14 < 0

 \therefore If E_{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) $[FeCl_4]^-$ 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 $[Cu(CN)_4]^{3-1}$

Answer (A,B,D)

Sol. $[\operatorname{FeCl}_4]^- \to \operatorname{Fe}^{3+}, 3d^5$ (weak field ligand) = sp^3 $[\operatorname{Fe}(\operatorname{CO})_4]^{-2} \to \operatorname{Fe}^{2-}, 3d^{10} \to sp^3$ $[\operatorname{Co}(\operatorname{CO})_4]^- \to \operatorname{Co}^-, 3d^{10} \to sp^3$ $[\operatorname{CoCl}_4]^{2-} \to \operatorname{Co}^{2+}, 3d^7$ (weak field ligand) $\to sp^3$ $[\operatorname{Ni}(\operatorname{CO})_4] \to \operatorname{Ni}, 3d^{10} \to sp^3$ $[\operatorname{Ni}(\operatorname{CN})_4]^{2-} \to \operatorname{Ni}^{2+}, 3d^8$ (strong field ligand) $\to dsp^2$ $[\operatorname{Cu}(\operatorname{py})_4]^+ \to \operatorname{Cu}^+, 3d^{10} \to sp^3$ $[\operatorname{Cu}(\operatorname{CN})_4]^{3-} \to \operatorname{Cu}^+, 3d^{10} \to sp^3$

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. $4H_3PO_3 \xrightarrow{\Lambda} PH_3 + 3H_3PO_4$

In H_3PO_4 , phosphorous is present in highest oxidation state, i.e., +5. So H_3PO_4 cannot acts 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.

- 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 cm² mol⁻¹. At 298 K, for an aqueous solution of the acid the degree of dissociation is α and the molar conductivity is $y \times 10^2$ S cm² mol⁻¹. At 298 K, upon 20 times dilution with water, the molar conductivity of the solution becomes $3y \times 10^2$ S cm² 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 × 10² S cm² 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

$$\alpha_{2} = \frac{\Lambda_{m}^{c_{2}}}{\Lambda_{m}^{\infty}} = \frac{3y \times 10^{2}}{4 \times 10^{2}} = \frac{3y}{4} \qquad \begin{bmatrix} c_{2} = \frac{c_{1}}{20} \end{bmatrix}$$

$$\frac{\alpha_{1}}{\alpha_{2}} = \frac{1}{3} \qquad \Rightarrow \quad \alpha_{2} = 3\alpha_{1}$$

$$HX \qquad \longleftrightarrow \qquad H^{+} + X^{-}$$

$$c_{1}(1-\alpha_{1}) \qquad c_{1}\alpha_{1} \qquad c_{1}\alpha_{1}$$

$$K_{a} = \frac{c_{1}\alpha_{1}^{2}}{1-\alpha_{1}} = \frac{c_{2}\alpha_{2}^{2}}{1-\alpha_{2}} = \frac{c_{1}(3\alpha_{1})^{2}}{20(1-3\alpha_{1})}$$

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

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

 $y = 4\alpha_1 = 0.86$

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 _____.

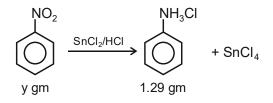
Answer (3.57)

10. The value of y is _____.

Answer (1.23)

Sol. Solution of Question Nos. 9 and 10

 $Sn + HCI \rightarrow SnCl_2$



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

- \Rightarrow Moles of nitrobenzene = 0.01
- \Rightarrow y = 0.01 × Molar mass of nitrobenzene

Also

No. of eq. of nitrobenzene = No. of eq. of $SnCl_2$

$$6 \times (0.01) = 2 \times n_{SnCl_2}$$
$$n_{SnCl_2} = 0.03$$
$$\implies n_{Sn} = 0.03$$

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 KMnO₄ solution to reach the end point. Number of moles of Fe²⁺ present in 250 mL solution is $x \times 10^{-2}$ (consider complete dissolution of FeCl₂). 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

8H⁺ + 5Fe²⁺ + MnO₄⁻ \rightarrow 5Fe³⁺ + Mn²⁺ + 4H₂O For 25 ml, meq of Fe²⁺ = meq of MnO₄⁻

For 250 ml,

mmoles of Fe²⁺ =
$$\frac{12.5 \times 0.03 \times 5 \times 250}{25}$$

moles of Fe²⁺ =
$$\frac{18.75}{1000}$$
 mol
= 18.75 × 10⁻³ mol
= 1.875 × 10⁻² mol
x = 1.875

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

% 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:

 $H_{3}C - H(g) \longrightarrow H_{3}C(g) + H(g) \Delta H^{\circ} = 105 \text{ kcal mol}^{-1}$ $CI - CI(g) \longrightarrow CI(g) + CI(g) \Delta H^{\circ} = 58 \text{ kcal mol}^{-1}$ $H_3C - Cl(g) \longrightarrow H_3C'(g) + Cl'(g) \Delta H^\circ = 85 \text{ kcal mol}^{-1}$

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

| | | Column J | Column K | |
|------|--------|---|------------------|-------------------------------------|
| | | Molecule | | BDE (kcal mol ⁻¹) |
| | (P) | H-C H(CH ₃) ₂ | (i) | 132 |
| | (Q) | H-CH ₂ Ph | (ii) | 110 |
| | (R) | H-CH=CH ₂ | (iii) | 95 |
| | (S) | H-C ≡CH | (iv) | 88 |
| | (A) | P - iii, Q - iv, R - i | i, S | — i |
| | (B) | P - i, $Q - ii$, $R - iii$, | , S - | - iv |
| | (C) | P-iii,Q-ii,R-i, | , S - | - iv |
| | (D) | P - ii, Q - i, R - iv, | , S - | - iii |
| Answ | ver (A | A) | | |
| Sol. | H – | $CH(CH_3)_2 \longrightarrow I$ | HĊ I Cŀ | – CH ₃ 1 ₃ |
| | Н – | $CH_2Ph \longrightarrow Ch$ | H ₂ – | Ph |

- $H CH = CH_2 \rightarrow {}^{\bullet}CH = CH_2$
- $H C \equiv CH \rightarrow {}^{\bullet}C \equiv CH$

Order of stability of free radical

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

:. Order of bond energy :

S > R > P > Q

14. For the following reaction

 $CH_4(g) + CI_2(g) \xrightarrow{\text{light}} CH_3CI(g) + HCI(g)$

the correct statement is

- (A) Initiation step is exothermic with $\Delta H^{\circ} = -58$ kcal mol⁻¹
- (B) Propagation step involving ${}^{\circ}CH_3$ formation is exothermic with $\Delta H^{\circ} = -2$ kcal mol⁻¹
- (C) Propagation step involving CH₃Cl formation is endothermic with ΔH° = +27 kcal mol⁻¹
- (D) The reaction is exothermic with $\Delta H^{\circ} = -25 \text{ kcal mol}^{-1}$

Answer (D)

Sol. (1) $Cl_2 \rightarrow 2Cl^{\bullet}$ (Initiation step) $\Delta H = 58$ kcal/mol

(2) $CH_4 + CI^{\bullet} \rightarrow {}^{\bullet}CH_3 + HCI$ (3) ${}^{\bullet}CH_3 + CI_2 \rightarrow CH_3CI + CI^{\bullet}$ Step (1) \rightarrow Endothermic (bond breaking) Step (2) $\rightarrow \Delta H = 105 - 103$ = 2 kcal/mol (Endothermic)Step (3) $\rightarrow \Delta H = 58 - 85$ = -27 kcal/mol (Exothermic)For complete reaction

$$\begin{split} & \mathsf{CH}_4(\mathsf{g}) + \mathsf{Cl}_2(\mathsf{g}) \overset{\text{light}}{\longrightarrow} \mathsf{CH}_3\mathsf{Cl}(\mathsf{g}) + \mathsf{HCl}(\mathsf{g}) \\ & \Delta\mathsf{H} = 58 + 105 - 85 - 103 \\ & = -25 \text{ kcal/mol} \end{split}$$

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 NaNO₃, 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 ₂ Fe[Fe(CN) ₆] | (D) | KFe[Fe(CN) ₆] |

Answer (C)

- 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(H₂O)₄]³⁺
 - (C) [Fe(NO)₄(SO₄)₂]
 - (D) $[Fe(NO)(H_2O)_5]^{2+}$

Answer (D)

Sol. Solution of Question Nos. 15 and 16

$$Fe^{2+} + K_{3}[Fe(CN)_{6}] \rightarrow Fe_{3}[Fe(CN)_{6}]_{2} \downarrow_{Turnbull's blue ppt.}$$

$$Fe^{2+} + K_{4}[Fe(CN)_{6}] \xrightarrow{\text{in absence}}_{\text{of air}} K_{2}Fe[Fe(CN)_{6}] \downarrow_{White ppt. (X)}$$
In air Fe²⁺ gets oxidised to Fe³⁺

$$Fe^{3+} + [Fe(CN)_{6}]^{4-} \longrightarrow Fe_{4}[Fe(CN)_{6}]_{3} \downarrow_{Prussian blue}$$

$$2NO_{3}^{-} + 4H_{2}SO_{4} + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2NO^{\uparrow} + 4SO_{4}^{2-} + 4H_{2}O^{\downarrow}_{Compound responsible}$$

$$[Fe(H_{2}O)_{6}]^{2+} + NO \longrightarrow [Fe(H_{2}O)_{5}NO]^{2+} + H_{2}O^{\downarrow}_{Compound responsible}$$

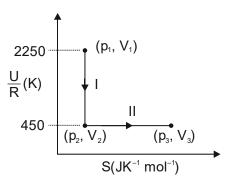
$$\therefore X = K_{2}Fe[Fe(CN)_{6}]$$
Brown ring is due to $[Fe(H_{2}O)_{5}NO]^{2+}$

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)

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

$$\Delta U = -1800R$$

$$W_{1} = \Delta U = -1800R$$
Process II - (Reversible Isothermal Process)

$$T_{1} = 900 \text{ K}$$
Calculation of T_{2} after reversible adiabatic process

$$-1800R = nC_{v}(T_{2} - T_{1})$$

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

$$T_{2} = 180 \text{ K}$$

$$W_{II} = -nRT_{2} \ln \frac{V_{3}}{V_{2}} = W_{I}$$

$$\Rightarrow -1 \times R \times 180 \ln \frac{V_{3}}{V_{2}} = -1800R$$

$$\ln \frac{V_{3}}{V_{2}} = 10$$

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)

Answer (30)

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

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

$$\therefore \quad \mathbf{m} \Delta \mathbf{v} = \mathbf{N}_{\mathbf{A}} \times \frac{\mathbf{h}}{\lambda}$$

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

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

 \therefore Change in velocity of He-atoms = 30 cm s⁻¹

19. Ozonolysis of CIO₂ 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 . $2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$

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