PART II: CHEMISTRY

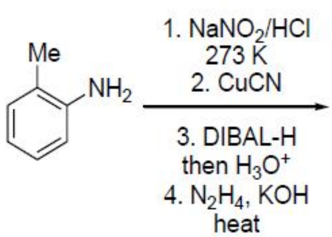
SECTION 1

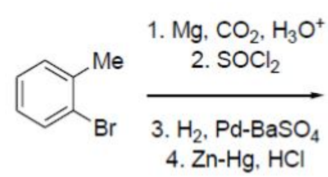
- This section contains **SIX (06)** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONE OR MOER THAN ONE** of these four option(s) is (are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will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

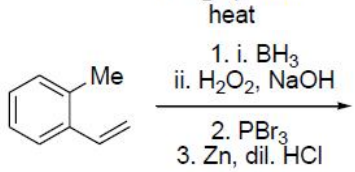
Full Mark	:	+4	If only (all) the correct option(s) is(are) chosen;
Partial Marks	:	+3	If all the four options are correct but ONLY three options are chosen;
Partial Marks	:	+2	If three or more options are correct but ONLY two options are chosen, both of which are correct;
Partial Marks	:	+1	If two or 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.

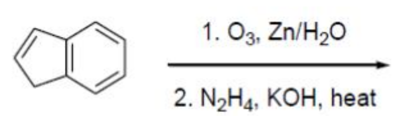
- For example, in a question, if (A), (B) and (D) are the ONLY three options corresponding to correct answers, then
  choosing ONLY (A), (B) and (D) will get +4 marks;
  choosing ONLY (A) and (B) will get +2 marks;
  choosing ONLY (A) and (D) will get +2 marks;
  choosing ONLY (B) and (D) will get +2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

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

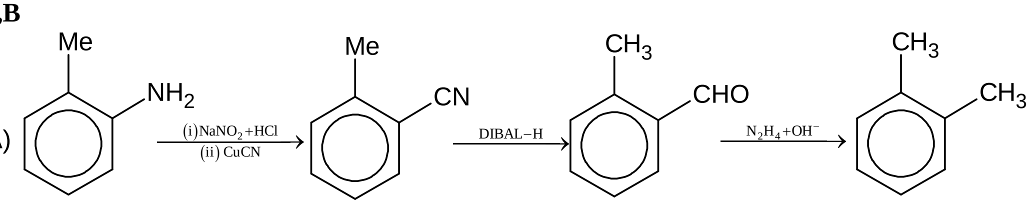
(A) 

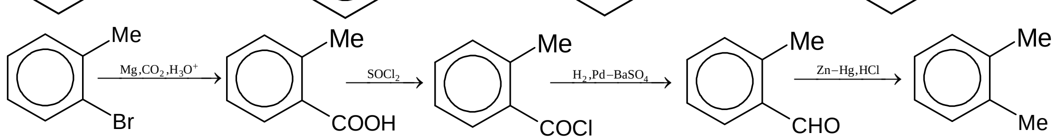
(B) 

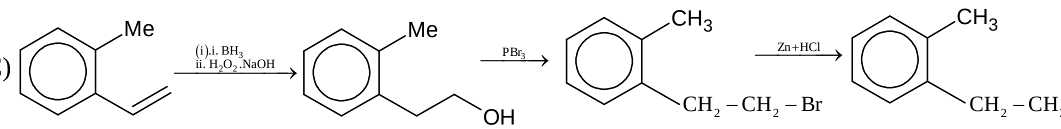
(C) 

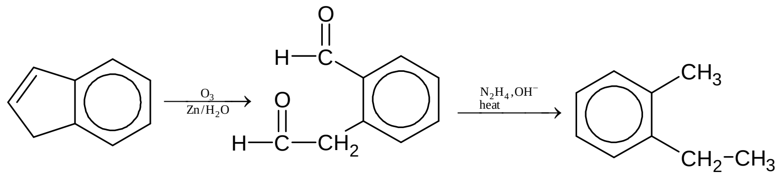
(D) 

Sol.: **A,B**

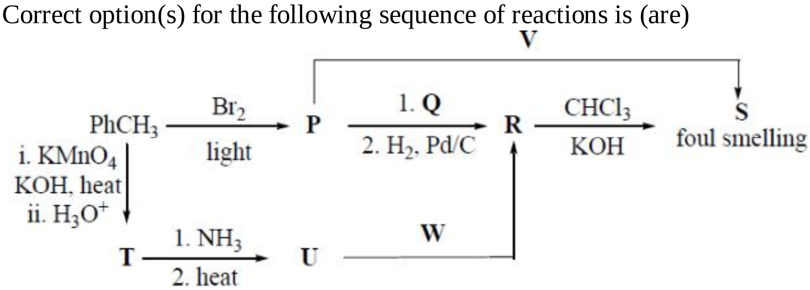
(A) 

(B) 

(C) 

(D) 

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



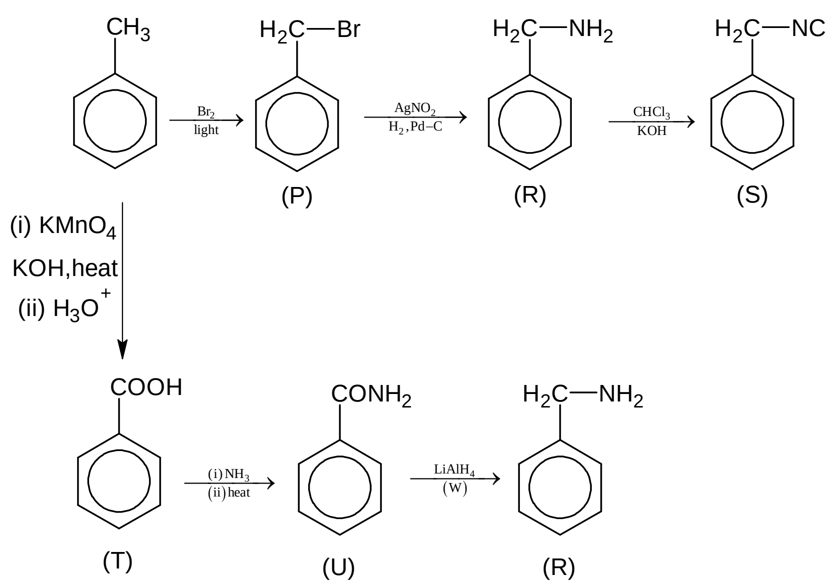
(A) $Q = KNO_2, W = LiA1H_4$

(B) R=benzenamine, V = KCN

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

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

Sol.: **C, D**



*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: 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 50s

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

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

Sol.: **B,C,D**

	2X	+	y	$\longrightarrow$	P
$t=0$	2		1		0
$t=50$	$2-2\times0.5$		$1-0.5$		
	1mole		0.5		

$$\text{rate} = -\frac{1}{2}\frac{dx}{dt} = -\frac{dy}{dt} = \frac{dP}{dt} = K[X]$$

$$-\frac{1}{2}\frac{dx}{dt} = K[X]$$

$$-\frac{dx}{dt} = 2K[X] = K^1[X]$$

Half life is t = 50 sec

$$2K = \frac{0.653L}{50}$$

$$K = \frac{0.6932}{100} = 6.332 \times 10^{-3}$$

t =50 sec

$$-\frac{dx}{dt} = 2K[X]$$

$$-\frac{dx}{dt} = 2 \times 6.332 \times 10^{-3} \times 1 = 13.864 \times 10^{-3} \text{ mole / L / Sec}$$

$$-\frac{dy}{dt} = K[X] = 6.332 \times 10^{-3}\left(\frac{1}{2}\right) = 3.46 \times 10^{-3} \text{ mole / L / Sec}^{-1}$$

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

Sol.: **A,B,C**

(A) $Cd + Ni^{+2} \longrightarrow Cd^{+2} + Ni$

$$E_{cell} = 0.40 + (-24) - \frac{0.0591}{2}\log\frac{0.001}{0.1}$$

$$= 0.16 + \frac{0.0591}{2} \times 2 = 6.64 + 0.551 = 0.71(+ve)$$

(B) $$E_{cell} = 0.40 + (-0.44) - \frac{0.591}{2}\log\frac{0.01}{0.1}$$

$$= -0.04 + \frac{0.591}{2} \times 2 = -0.04 + 0.06 = 0.02(+ve)$$

(C) $$E_{cell} = 0.24 + (-0.13) + \frac{.0591}{2} \times 2$$

$$= 0.11 + 0.06 = 0.33(+ve)$$

(D) $$E_{cell} = 0.24 + (-0.44) + \frac{0.0591}{2} \times 2$$

$$= -0.20 + 0.06 = -0.14(-ve)$$

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

Sol.: **A, B, D**

(A) $[FeCl_4]^-$

$Fe^{+3} = 3d^5, Cl^-$ weak field liganol sp^3

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

$Fe^{-2} = 3d^8 4s^2$

CO strong field liganol pairing occurs

$Fe^{-2} = 3d^{10}$ hence sp^3

(B) $[Co(CO)_4]^-$

$Co = 3d^8 4s^2$ due to CO pairing occurs

Hence = $3d^{10}$

$[CoCl_4]^{-2}$

$Co^{+2} = 3d^7$, Cl^- weak field liganol sp^3

(D) $[Cu(Py)_4]^{+1}$

$Cu^{+1} = 3d^{10}$, sp^3

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

$Cu^{+1} = 3d^{10}$, sp^3

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.

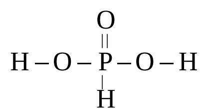
(B) While H_3PO_3 can act as reducing agent, H_3PO_4 cannot.

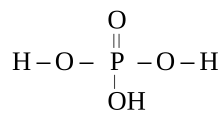
(C) H_3PO_3 is a monobasic acid.

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

Sol.: **A,B,D**

$$H_3PO_3 \xrightarrow{\Delta} H_3PO_4 + PH_3$$





P–H bond is responsible for it is reducing character, H_3PO_4 doesnot have.

H_3PO_3 is a dibasic acid in oxyacids of phosphors O–H bond is ionisalbe where as P–H bond is non ionizable.

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 Mark	:	+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 $y \times 10^2 \text{S cm}^2\text{mol}^{-1}$. 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 _______.

Sol.: **0.22**

$$\alpha_1 = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{y \times 10^2}{4 \times 10^2} = \frac{y}{4} = \alpha$$

On dilution conductivity increases three times

$$\alpha_2 = \frac{3y \times 10^2}{4 \times 10^2} = 3\alpha_1 = 3\alpha$$

HA	$\rightleftharpoons$	H^+	+	A^-
C		O		O
$C(1-\alpha)$		$C\alpha$		$C\alpha$

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

Since temperature is constant K_a will be constant

$$\frac{C_1\alpha_1^2}{1-\alpha_1} = \frac{C_2\alpha_2^2}{1-\alpha_2}$$

$$\frac{C\times\alpha^2}{1-\alpha} = \frac{\left(\frac{C}{20}\right)(3\alpha)^2}{1-3\alpha}$$

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

$$20 - 60\alpha = 9 - 9\alpha;$$

$$\alpha = \frac{11}{51} = 0.2156$$

$$\alpha = 0.22$$

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

Sol.: **0.88**

$$\alpha = \frac{y}{4}; \quad y = 4\alpha = 4\times 0.22 = 0.88$$

Question Stem for Question Nos. 9 and 10

Question Stem

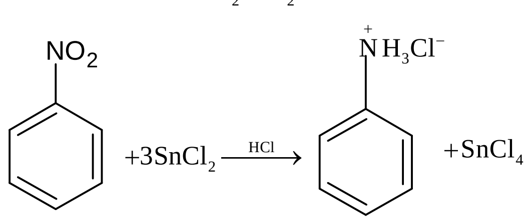
Reaction of **x** g of Sn with HCl quantitatively produced a salt. Entire amount of the salt reacted with **y** g of nitrobenzene in the presence of required amount of HCl to produce 1.29 g of an organic salt (quantitatively).

(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 _______.

Sol.: **3.57**

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2$$



Moles of $Sn = \frac{x}{119}$

Moles of nitrobenzene = $\frac{x}{119}\times\frac{1}{3}$

Moles of anilium chloride $= \frac{x}{119}\times\frac{1}{3}$

Moles of nitrobenzene $= \frac{x}{357}$

$$\frac{y}{123} = \frac{x}{357} \quad \ldots (1)$$

Moles of anilium chloride $= \frac{x}{357}$ … (2)

$$\frac{1.29}{129} = \frac{x}{357}$$

x = 3.57

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

Sol.: **1.23**

$y = 1.225 \cong 1.23$

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 _______.

Sol.: **1.875**

meq of Fe^{+2} = meq of $KMnO_4$

$x \times 10^{-2} \times 1000 \times 1 = 12.5 \times 0.03 \times 5 \times 10$

x = 1.875 mole

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

Sol.: **18.75**

Moles of $Fe^{+2} = x \times 10^{-2} = 1.875 \times 10^{-2}$

wt.of $Fe^{+2} = 1.875 \times 10^{-2} \times 56$

Hence percentage of Fe^{+2}

$$= \frac{1.875 \times 10^{-2} \times 56}{5.6} \times 100\% = 18.75\%$$

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 Mark	:	+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:

$$H_3C{-}H(g) \longrightarrow H_3C^{\bullet}(g) + H^{\bullet}(g) \quad \Delta H^{o} = 105 \text{ kcal mol}^{-1}$$

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

$$H_3C{-}Cl(g) \longrightarrow H_3C^{\bullet}(g) + Cl^{\bullet}(g) \quad \Delta H^{o} = 85 \text{ kcal mol}^{-1}$$

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

*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 (kcl mol^{-1})
(P) $H-CH(CH_3)_2$	(i) 132
(Q) $H-CH_2Ph$	(ii) 110
(R) $H-CH=CH_2$	(iii) 95
(S) $H-C\equiv CH$	(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

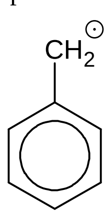
(D) P – ii, Q – i, R – iv, S – iii

Sol.: **A**

As S character increases bond dissociation energy increases

$H-C\equiv CH$ (sp) $\quad H-CH=CH_2$ (sp^2)

$H-CH(CH_3)_2$ (sp^3) $\quad H-CH_2-Ph$ (sp^3)

And  is more stable then $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C^{\odot}}}$

*14. For the following reaction

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

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}.

Sol.: **D**

$CH_4 + Cl_2 \xrightarrow{\text{light}} CH_3Cl + HCl$ this reaction is obtained from given reaction.

$CH_3 - H \longrightarrow CH_3^{\odot} + H^{\odot}$ ...(1)

$Cl - Cl \longrightarrow Cl^{\odot} + Cl^{\odot}$ ...(2)

$CH_3 - Cl \longrightarrow CH_3^{\odot} + Cl^{\odot}$ ...(3)

$H - Cl \longrightarrow H^{\odot} + Cl^{\odot}$ ...(4)

$(1)+(2)-(3)-(4)$

Hence $\Delta H = 105 + 58 - 85 - 103 = -25$ KCal / mole

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) $KFe[Fe(CN)_6]$

Sol.: **C**

$FeSO_4 + K_4[Fe(CN)_6] \longrightarrow K_2Fe[Fe(CN)_6]$

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

Sol.: **D**

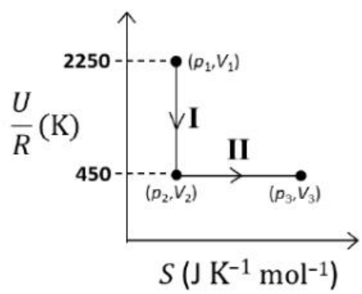
$FeSO_4 + NaNO_3 + H_2SO_4 \longrightarrow [Fe(H_2O)_5 NO]^{+2} + SO_4^{-2}$

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 designed to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

Full Mark	:	+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 process are same, the value of ln $\frac{V_3}{V_2}$ ___



(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 $\frac{5}{2}R$)

Sol.: **10**

1 st process is adiabatic since entropy is constant.

$W_1 = \Delta U$

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

$W_1 = -1800R$ … (1)

In 2nd process internal energy is constant it means it is a isothermal process.

$W_2 = -2.303nRT\log\frac{V_3}{V_2}$ ….(2)

$= -nRT\ln\frac{V_3}{V_2}$ ….(3)

Given, n = 1 mole, here temperature is unknown

$U = nC_V T$ for process II

$450R = 1\times\frac{5}{2}RT$

$T = \frac{450\times 2}{5} = 180K$

Equation (1) = equation (2)

$W_1 = W_2$

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

$\ln\frac{V_3}{V_2} = \frac{1800}{180} = 10$

*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})

Sol.: **30**

$$\lambda = \frac{h}{m(\Delta V)}$$

$$330 \times 10^{-9} = \frac{6.6 \times 10^{-34}}{\left(\frac{4 \times 10^{-3}}{6 \times 10^{23}}\right) \times \Delta V}$$

$$\Delta V = \frac{6.6 \times 6 \times 10^{23} \times 10^{-34}}{4 \times 10^{-3} \times 330 \times 10^{-9}}$$

$$= 0.30 \text{ m/s}$$

$$= 0.30 \times 100 \text{ cm/s}$$

$$= 30 \text{ cm/s}$$

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

Sol.: **6**

$$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$$

Average oxidization state of Cl atom is +6