QUESTIONS & KEYS FOR JEE (ADVANCED)-2021 (PAPER 2)

[CHEMISTRY]

SECTION 1

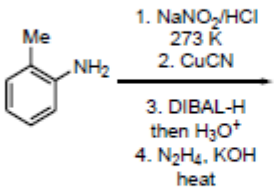
- This section contains **SIX (06)** question.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will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

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 correction option.
Zero Marks	:	0	If unanswered;
Negative Marks	:	−2	In all other cases.

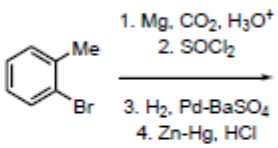
- For example, in a question, if (A), (B) and (D) are the ONLY options corresponding to correct answers, then
  Choosing ONLY (A), (B) and (D) will get +4 marks;
  Choosing ONLY (A) and (B) will get +2 marks;
  Choosing ONLY (A) and (D) will get +2 marks;
  Choosing ONLY (B) and (D) will get +2 marks;
  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 questions is unanswered) will get 0 marks and
  choosing any other option(s) will get −2 marks.

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

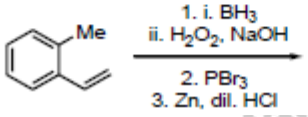
(A)



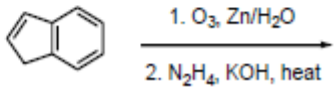
(B)



(C)

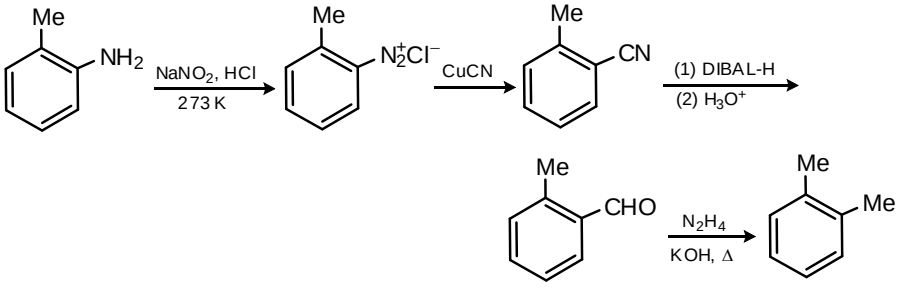


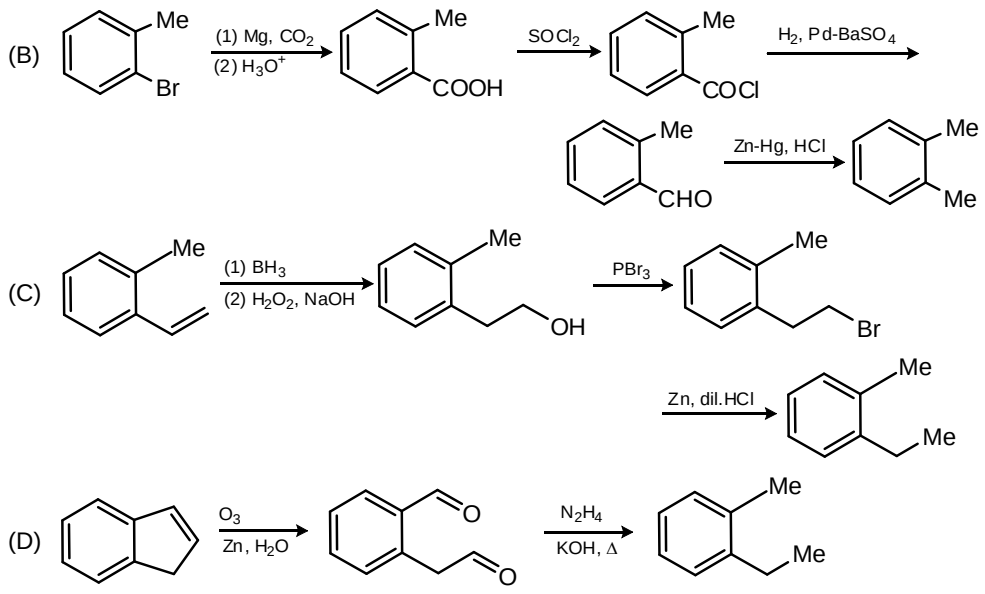
(D)



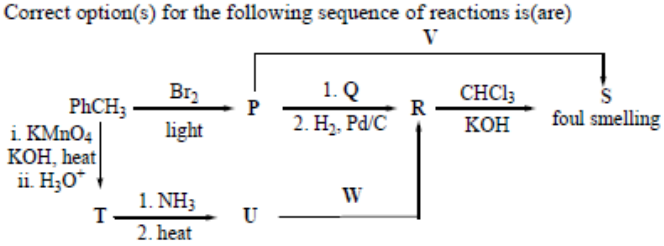
Answer Key (A, B)

Sol: (A)





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

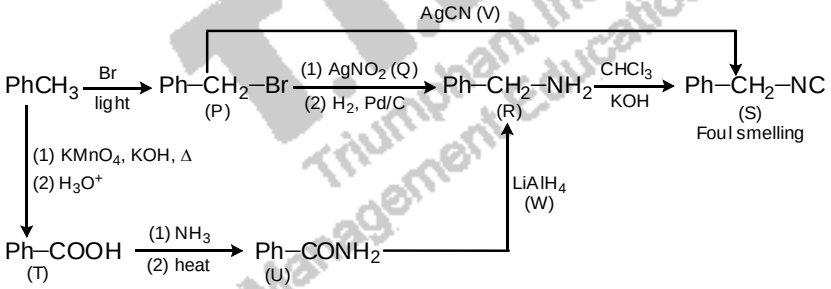


(A) **Q** = KNO_2, **W** = $LiAlH_4$ (B) **R** = benzenamine, **V** = KCN

(C) **Q** = $AgNO_2$, **R** = phenylmethanamine (D) **W** = $LiAlH_4$, **V** = AgCN

Answer Key (C, D)

Sol:



Q.3 For the following reaction

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

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

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

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

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

Answer Key (B, C, D)

Sol: $\frac{dp}{dt} = k[x]^1$

	$2x$	+	$y \rightarrow$	p
$t = 0$	2		1	
$t = 50$ s	1		0.5	0.5

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

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

$\ln [X_0] - \ln [X_t] = 2kt$

$2k \times 50 = \ln 2$

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

At 50 s, $\frac{-d[X]}{dt} = 2k \times (1) = 2 \times 6.93 \times 10^{-3}$

$= 13.86 \times 10^{-3}$

At 100 s, $\frac{-1}{2}\frac{d[X]}{dt} = \frac{-d[Y]}{dt}$

$$\frac{-d[Y]}{dt} = k \times \frac{1}{2} = 3.46 \times 10^{-3}$$

Q.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 Key (A, B, C)

Sol: $X_{(s)} + Y^{2+}_{(0.1M)} \rightarrow X^{2+}_{(0.001M)} + Y_{(s)}$

$$E_{cell} = E^{o}_{cell} - \frac{0.06}{2}\log\frac{X^{2+}}{Y^{2+}} = E^{o}_{cell} - \frac{0.06}{2}\log\frac{10^{-3}}{10^{-1}}$$

$$E_{cell} = E^{o}_{cell} + 0.06$$

(A) $E^{o}_{cell} = (-0.24) - (-0.4) = 0.16$ V and $E_{cell} = 0.22$ V

(B) $E^{o}_{cell} = (-0.44) - (-0.40) = -0.04$ V and $E_{cell} = -0.04 + 0.06 = 0.02$ V

(C) $E^{o}_{cell} = (-0.13) - (-0.24) = 0.11$ V and $E_{cell} = 0.17$ V

(D) $E^{o}_{cell} = (-0.44) - (-0.24) = -0.20$ V and $E_{cell} = -0.20 + 0.06 = -0.14$ V

Combinations in (A), (B) and (C) gives positive values

Q.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 $[CoCl_4]^{2-}$

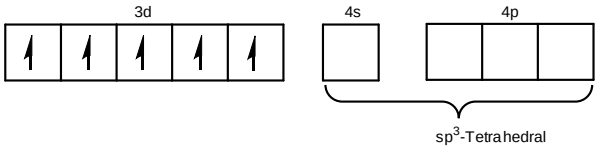
(C) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ (D) $[Cu(py)_4]^+$ and $[Cu(CN)_4]^{3-}$

Answer Key (A, B, D)

Sol: $[FeCl_4]^-$

Fe^{3+} [Ar] $3d^5$

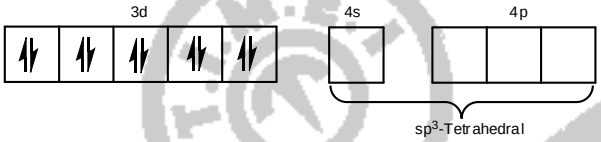
Since Cl^- is a weak field ligand pairing will not takes place



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

Fe^{2+} [Ar] $3d^8$ $4s^2$

CO is a strong field ligand and force the electrons of 4s subshell to occupy 3d subshell



$[Co(CO)_4]^-$

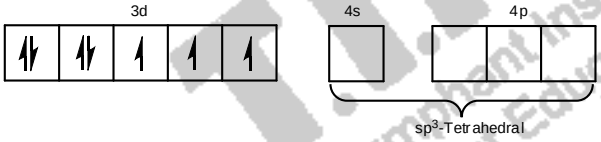
Co^-Ar] $3d^8$ $4s^2$

$\therefore$Similar to $[Fe(CO)_4]^{2-}$ hybridisation is sp^3

$[CoCl_4]^{2-}$

Co^{2+} [Ar] $3d^7$

Cl^- is a weak field ligand, electron pairing will not takes place



$[Ni(CO)_4]$

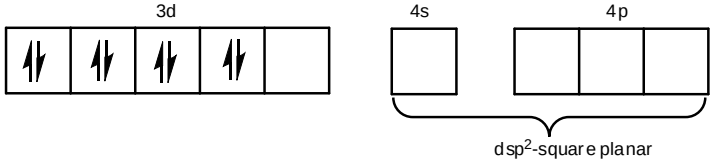
Ni[Ar] $3d^8$ $4s^2$

$\therefore$similar to $[Fe(CO)_4]^{2-}$ shape is tetrahedral

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

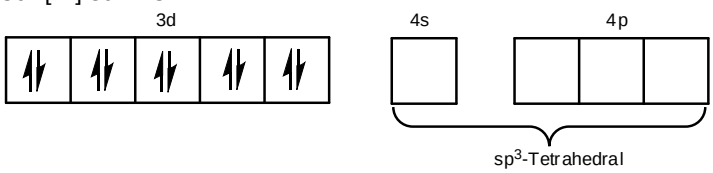
Ni^{2+} [Ar] $3d^8$

CN^- is a strong filed ligand, electron pairing takes place



$[Cu(Py)_4]^+$

Cu^+ [Ar] $3d^{10}$ $4s^0$



$[Cu(CN)_4]^{3-}$
Cu^+ [Ar] $3d^{10}$ $4s^0$
$\therefore$ Similar to $[Cu(Py)_4]^+$ shape is tetrahedral

Q.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.

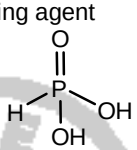
(C) H_3PO_3 is a monobasic acid.

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

Answer Key (A, B, D)

Sol: (A) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$

(B) In H_3PO_4, phosphorus in its highest oxidation state (+5)
$\therefore$ it cannot act as reducing agent

(C) H_3PO_3 is a dibasic acid, 

(D) Only those hydrogens attached to oxygen are ionisable

SECTION 2

- This section contains **THREE (03)** questions 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 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 No. 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}.

Q.7 The value of α is ___.

Answer Key (0.21)

Sol: $\alpha = \frac{\lambda_m}{\lambda_m^o}$

$\alpha = \frac{y}{4}$ and $\alpha'_{(\text{after dilution})} = \frac{3y}{4}$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{\frac{C}{20}\times(\alpha')^2}{1-\alpha'}$$

Substituting α and α' in terms of y

$$y = \frac{44}{51} = 0.86$$

$$\alpha = \frac{y}{4} = \frac{0.86}{4} = 0.21$$

Q.8 The value of y is ___.

Answer Key (0.86)

Sol: Solution is same as above

Question Stem for Question No. 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).

Q.9 The value of x is ___.

Answer Key (3.57)

Sol: $3Sn + 6HCl + C_6H_5NO_2 \longrightarrow C_6H_5NH_2 + 3SnCl_2 + 2H_2O$

$C_6H_5NH_2 \xrightarrow{HCl} C_6H_5NH_3^+Cl^-$

Molecular weight of organic salt $(C_6H_5NH_3^+Cl^-) = 129$ gm

1.29 g of organic salt require 0.01 mole nitrobenzene

$\therefore$ The amount of nitrobenzene = $0.01 \times 123 = 1.23$ g

No. of moles of Sn = 0.03

$\therefore$ The amount of nitrobenzene = $0.01 \times 357 = 3.57$ g

Q.10 The value of y is ___.

Answer Key (1.23)

Sol: Solution is same as above

Question Stem for Question No. 11and 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})

Q.11 The value of x is ___.

Answer Key (1.87)

Sol: $Fe + 2HCl \rightarrow FeCl_2 + H_2$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (n factor = 1)

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (n factor = 5)

$[Fe^{2+}] \times 25 = 0.03 \times 5 \times 12.5$

$[Fe^{2+}] = 0.075$

Number of moles of $Fe^{2+} = \frac{0.075 \times 250}{1000} = 1.87 \times 10^{-2}$

Value of x = 1.87

Q.12 The value of y is ___.

Answer Key (18.75)

Sol: Weight of Fe in the sample = $1.87 \times 10^{-2} \times 56 = 1.05$

$\%\ Fe = \frac{1.05}{5.6} \times 100 = 18.75$

Value of y = 18.75

SECTION 3

- This section contains **TWO (02) paragraph**s Based on each paragraph, there are **TWO (02)** questions.
- Each questions 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 <u>according to the following marking scheme.</u>

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:

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

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

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

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

Q.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–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

Answer Key (A)

Sol: Minimum bond enthalpy of C–H bond, maximum stability of the resulting free radical

$PhCH_2$–H forms $Ph-\dot{C}H_2$ which is the most stable carbocation due to resonance

$\therefore$ (Q) should match with (iv)

$CH{\equiv}C$–H forms $CH\equiv\dot{C}$ which is the least stable because of the highest s-character of the carbon

$\therefore$ (S) should match with (i)

Q.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}.

Answer Key (D)

Sol: The initial step $Cl_2 \rightarrow 2Cl^{\bullet}$ and propagation step $CH_4 + Cl^{\bullet} \rightarrow CH_3^{\bullet} + HCl$ are endothermic

While propagation step involving $CH_3^{\bullet} + Cl^{\bullet} \rightarrow CH_3Cl$ is exothermic

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.

Q.15 Precipitate **X** is

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

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

Answer Key (C)

Sol: $K_4[Fe(CN)_6] \xrightarrow[\text{absence of air}]{FeSO_4} \underset{\text{(white precipitate)}}{Fe[Fe(CN)_6]}$

$\xrightarrow{FeSO_4\ \text{(air)}}$

$\underset{\text{(Blue)}}{F_4[Fe(CN)_6]_3}$

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

Answer Key (D)

Sol: Brown ring formation is due to $[Fe(H_2O)_5NO]SO_4$

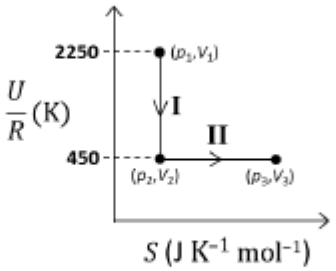
SECTION 4

- 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 <u>according to the following marking scheme.</u>

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

Zero Marks : 0 In all other cases.

Q.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 Key (10)

Sol: Since $q_I = 0$, $\Delta U_I = W_I = nC_v\Delta T$

$$-1800R = 1\times\frac{5}{2}R\times\Delta T$$

$\Delta T = -720$ K

$T_2 = 900 - 720 = 180$ K

Given $W_{II} = W_I = -1800\ R = -nRT\ \ln\left(\frac{V_3}{V_2}\right)$

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

$$\ln\left(\frac{V_3}{V_2}\right) = 10$$

Q.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})

Answer Key (30)

Sol: $$\lambda = \frac{h}{p} = \frac{h}{mv}$$

$$V = \frac{6.6\times10^{-34}\times6\times10^{23}}{330\times10^{-9}\times4\times10^{-3}} = 0.3\ ms^{-1} = 30\ cm\,s^{-1}$$

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

Answer Key (6)

Sol: $2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$

The average oxidation state of chlorine in Cl_2O_6 is 6.