Paper Specific Instructions

1. The examination is of 3 hours duration. There are a total of 60 questions carrying 100 marks. The entire paper is divided into three sections, **A**, **B** and **C**. All sections are compulsory. Questions in each section are of different types.

2. **Section – A** contains a total of 30 **Multiple Choice Questions (MCQ).** Each MCQ type question has four choices out of which only **one** choice is the correct answer. Questions Q.1 – Q.30 belong to this section and carry a total of 50 marks. Q.1 – Q.10 carry 1 mark each and Questions Q.11 – Q.30 carry 2 marks each.

3. **Section – B** contains a total of 10 **Multiple Select Questions (MSQ).** Each MSQ type question is similar to MCQ but with a difference that there may be **one or more than one** choice(s) that are correct out of the four given choices. The candidate gets full credit if he/she selects all the correct answers only and no wrong answers. Questions Q.31 – Q.40 belong to this section and carry 2 marks each with a total of 20 marks.

4. **Section – C** contains a total of 20 **Numerical Answer Type (NAT)** questions. For these NAT type questions, the answer is a real number which needs to be entered using the virtual keyboard on the monitor. No choices will be shown for these type of questions. Questions Q.41 – Q.60 belong to this section and carry a total of 30 marks. Q.41 – Q.50 carry 1 mark each and Questions Q.51 – Q.60 carry 2 marks each.

5. In all sections, questions not attempted will result in zero mark. In **Section – A** (MCQ), wrong answer will result in **NEGATIVE** marks. For all 1 mark questions, 1/3 marks will be deducted for each wrong answer. For all 2 marks questions, 2/3 marks will be deducted for each wrong answer. In **Section – B** (MSQ), there is **NO NEGATIVE** and **NO PARTIAL** marking provisions. There is **NO NEGATIVE** marking in **Section – C** (NAT) as well.

6. Only Virtual Scientific Calculator is allowed. Charts, graph sheets, tables, cellular phone or other electronic gadgets are **NOT** allowed in the examination hall.

7. The Scribble Pad will be provided for rough work.

SECTION – A

MULTIPLE CHOICE QUESTIONS (MCQ)

Q. 1 – Q.10 carry one mark each.

Q.1   The CORRECT order of pK_a for the compounds **I** to **IV** in water at 298 K is

$HCo(CO)_4$ $HCo(CO)_3(PPh_3)$ $HCo(CO)_3(P(OPh)_3)$ $HCo(CO)_2(PPh_3)_2$
   I   **II**   **III**   **IV**
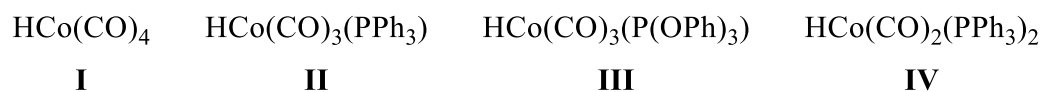
(A) **I** > **II** > **III** > **IV**   (B) **IV** > **III** > **II** > **I**

(C) **IV** > **II** > **III** > **I**   (D) **I** > **III** > **II** > **IV**

Q.2   For Na^+, Mg^{2+}, Al^{3+} and F^-, the CORRECT order of ionic radii is

(A) $Al^{3+} > Mg^{2+} > Na^+ > F^-$ (B) $Al^{3+} > Na^+ > Mg^{2+} > F^-$

(C) $F^- > Na^+ > Mg^{2+} > Al^{3+}$ (D) $Na^+ > F^- > Mg^{2+} > Al^{3+}$

Q.3   Spin-only magnetic moments (in BM) of $[NiCl_2(PPh_3)_2]$ and $[Mn(NCS)_6]^{4-}$, respectively, are

(A) 0.00 and 5.92   (B) 2.83 and 1.89

(C) 0.00 and 1.89   (D) 2.83 and 5.92

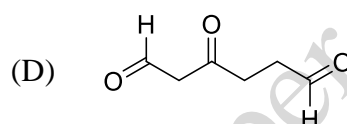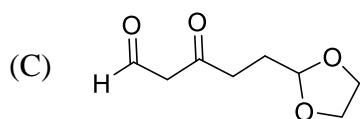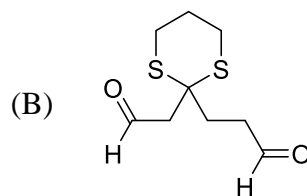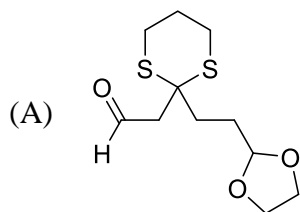Q.4   Two sets of quantum numbers with the same number of radial nodes are
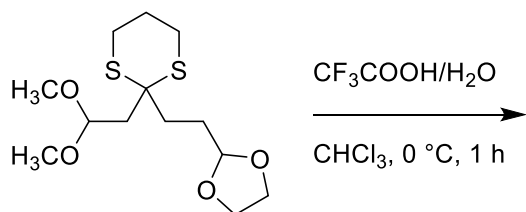
(A) n = 3; l = 0; m_l = 0   and   n = 2; l = 0; m_l = 0

(B) n = 3; l = 1; m_l = 1   and   n = 2; l = 1; m_l = 0

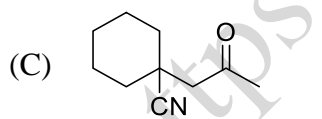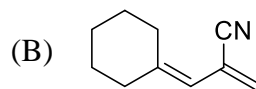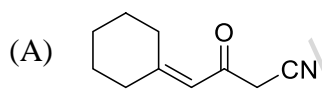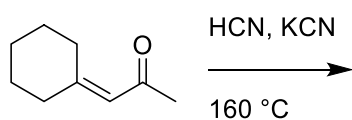(C) n = 3; l = 2; m_l = 0   and   n = 2; l = 1; m_l = 0

(D) n = 3; l = 1; m_l = −1   and   n = 2; l = 1; m_l = 0
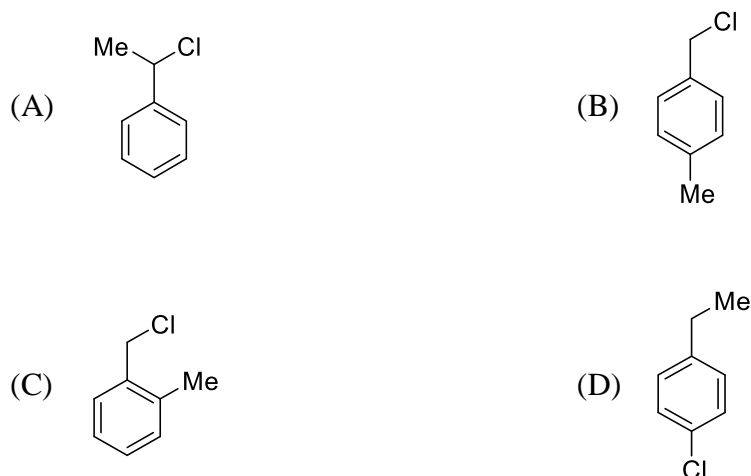
Q.5   The major product formed in the following reaction is

(A)   (B)

(C)   (D)

Q.6   The major product formed in the following reaction is

(A)   (B)

(C)   (D)
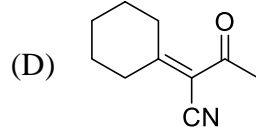
Q.7   A compound shows ^{1}H NMR peaks at δ-values (in ppm) 7.31 (2H), 7.21 (2H), 4.5 (2H) and 2.3 (3H). The structure of the compound is
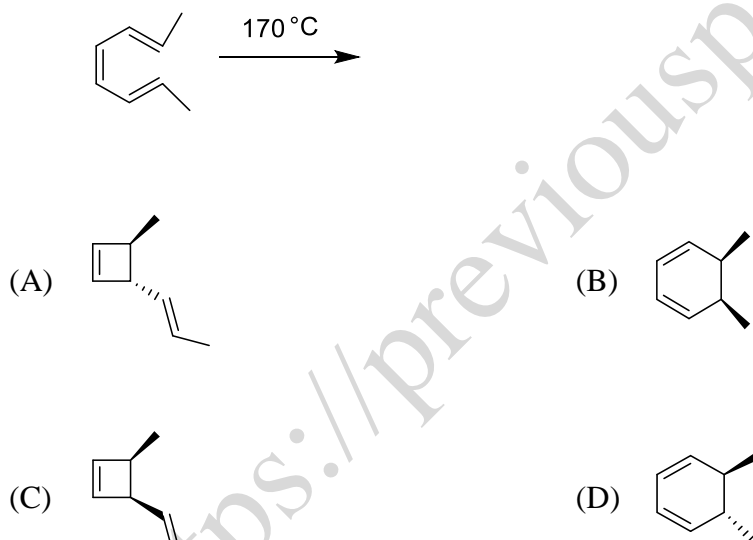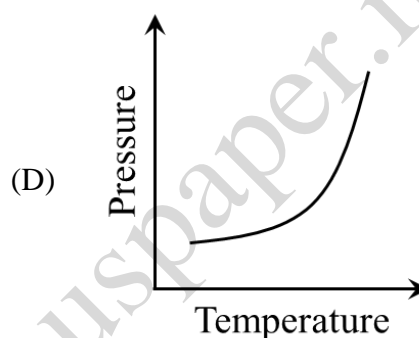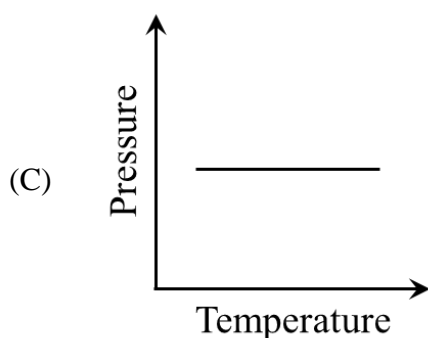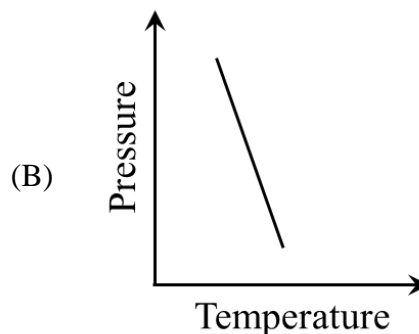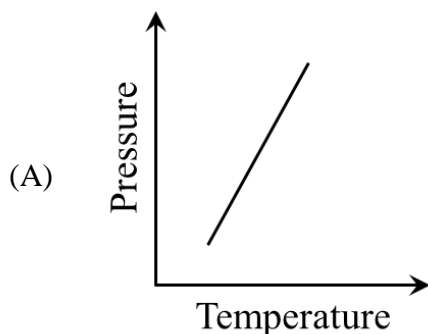
(A)

(B)

(C)

(D)

Q.8   The major product formed in the following reaction is

(A)

(B)

(C)

(D)

Q.9 A pure substance **M** has lesser density in solid state than in liquid state. The ΔS_{fusion} of **M** is $+25$ J K^{-1} mol^{-1}. The CORRECT representative Pressure-Temperature diagram for the fusion of **M** is

(A)

(B)

(C)

(D)

Q.10 Among the following, the matrices with non-zero determinant are

$$\mathbf{P} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad \mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 4 \end{bmatrix} \quad \mathbf{R} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 \\ 3 & 1 & 3 & 0 \\ 4 & 3 & 1 & 4 \end{bmatrix} \quad \mathbf{S} = \begin{bmatrix} 1 & 2 & 3 & 1 \\ 2 & 3 & 4 & 2 \\ 3 & 4 & 1 & 3 \\ 4 & 1 & 2 & 4 \end{bmatrix}$$

(A) **P**, **Q** and **R**

(B) **P**, **R** and **S**

(C) **P**, **Q** and **S**

(D) **Q**, **R** and **S**

Q. 11 – Q. 30 carry two marks each.

Q.11   Reaction of BCl_3 with NH_4Cl at 140 °C produces compound **P**. Further, **P** reacts with $NaBH_4$ to give a colorless liquid **Q**. The reaction of **Q** with H_2O at 100 °C produces compound **R** and a diatomic gas **S**. Among the following, the CORRECT statement is

(A) **P** is $B_3N_3H_6$

(B) **R** is $[B(OH)NH]_3$

(C) **Q** is $[BClNH]_3$

(D) **S** is Cl_2

Q.12   The complex that does **NOT** obey the 18-electron rule is
(*Given*: Atomic numbers of Ti, Mn, Ta and Ir are 22, 25, 73 and 77, respectively)

(A) $[(\eta^5\text{-}C_5H_5)Ti(CO)_4]^-$

(B) $[Mn(SnPh_3)_2(CO)_4]^-$

(C) $[(\eta^5\text{-}C_5H_5)Ir(CH_2)(PMe_3)]$

(D) $[TaCl_3(PEt_3)_2(CHCMe_3)]$

Q.13   Hybridization of the central atoms in I_3^-, ClF_3 and SF_4, respectively, are

(A) sp^3d, sp^2 and dsp^2

(B) sp, sp^3d and dsp^2

(C) sp^3d, sp^3d and sp^3d

(D) sp, sp^2 and sp^3d

Q.14   Reaction of $[Ni(CN)_4]^{2-}$ with metallic potassium in liquid ammonia at −33 °C yields complex **E**. The geometry and magnetic behavior of **E**, respectively, are

(A) Square planar and diamagnetic

(B) Tetrahedral and diamagnetic

(C) Octahedral and paramagnetic

(D) Square pyramidal and paramagnetic

Q.15   The decreasing order of C=C bond length in the following complexes is
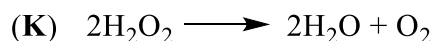
$[Cl_3Pt(CH_2=CH_2)]^-$ $[Cl_3Pt(C(CN)_2=C(CN)_2)]^-$ $[Cl_3Pt(CF_2=CH_2)]^-$ $[Cl_3Pt(CF_2=CF_2)]^-$
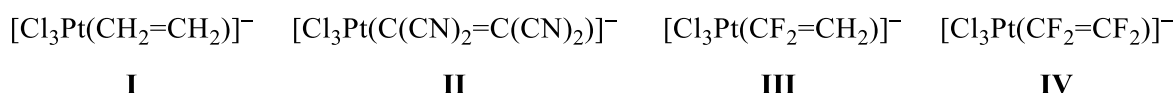
  I   **II**   **III**   **IV**

(A) **II** > **III** > **IV** > **I**

(B) **IV** > **II** > **III** > **I**

(C) **II** > **IV** > **III** > **I**

(D) **IV** > **II** > **I** > **III**

Q.16 The CORRECT combination for metalloenzymes given in **Column I** with their catalytic reactions in **Column II** is
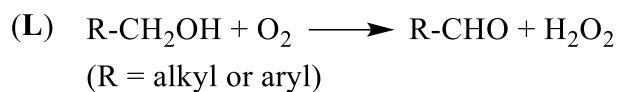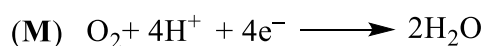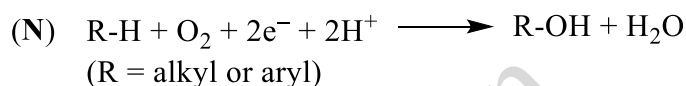
Column I

(i) Cytochrome P-450

(ii) Catalase

(iii) Galactose oxidase

(iv) Cytochrome c oxidase

Column II

(**K**) $2H_2O_2 \longrightarrow 2H_2O + O_2$

(**L**) $R\text{-}CH_2OH + O_2 \longrightarrow R\text{-}CHO + H_2O_2$
(R = alkyl or aryl)

(**M**) $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

(**N**) $R\text{-}H + O_2 + 2e^- + 2H^+ \longrightarrow R\text{-}OH + H_2O$
(R = alkyl or aryl)

(A) (i)−(**M**); (ii)−(**N**); (iii)−(**K**); (iv)–(**L**)

(B) (i)–(**N**); (ii)–(**L**); (iii)–(**K**); (iv)–(**M**)

(C) (i)–(**N**); (ii)–(**K**); (iii)–(**L**); (iv)–(**M**)

(D) (i)–(**M**); (ii)–(**K**); (iii)–(**L**); (iv)–(**N**)

Q.17 According to the crystal field theory, d–d transition observed in $[Ti(H_2O)_6]^{3+}$ is

(A) Laporte forbidden and spin forbidden

(B) Laporte allowed and spin forbidden

(C) Laporte allowed and spin allowed

(D) Laporte forbidden and spin allowed

Q.18   The major product formed in the following reaction sequence is

1. [diethyl malonate], NaOEt

2. $(CH_3)_2NH$

3. $LiAlH_4$

4. BF_3, HCHO

(A)

(B)

(C)

(D)
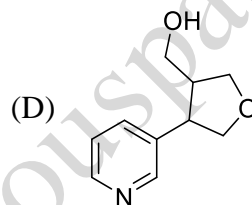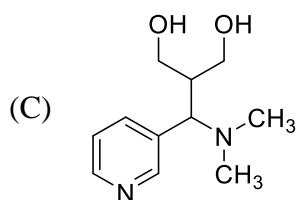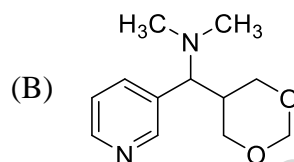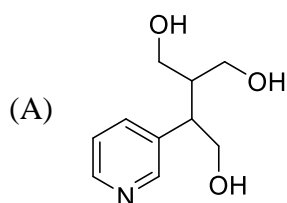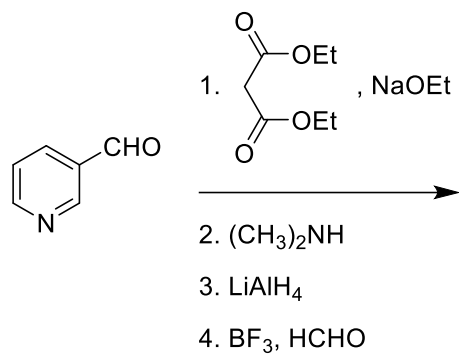
Q.19   The products **P**, **Q**, **R** and **S** formed in the following reactions are
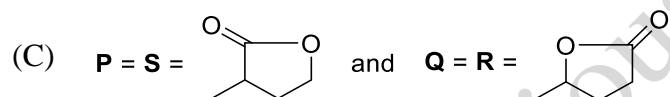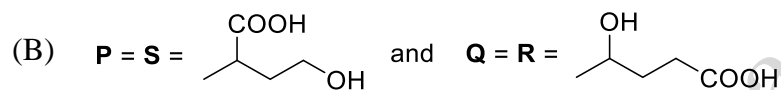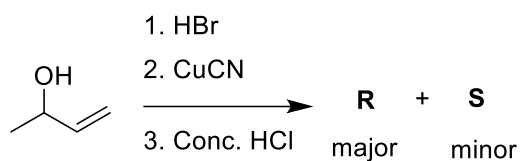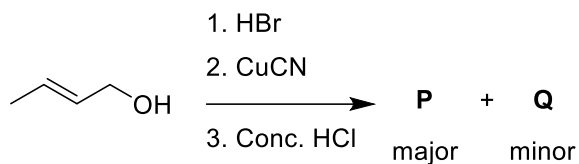
$$\text{CH}_3\text{CH=CHCH}_2\text{OH} \xrightarrow[\substack{\text{3. Conc. HCl}}]{\substack{\text{1. HBr}\\\text{2. CuCN}}} \mathbf{P} \; + \; \mathbf{Q}$$

major   minor

$$\text{CH}_3\text{CH(OH)CH=CH}_2 \xrightarrow[\substack{\text{3. Conc. HCl}}]{\substack{\text{1. HBr}\\\text{2. CuCN}}} \mathbf{R} \; + \; \mathbf{S}$$

major   minor

(A)   **P** = **R** = CH$_3$CH=CHCH$_2$COOH (E-isomer)   and   **Q** = **S** = CH$_3$CH(COOH)CH=CH$_2$

(B)   **P** = **S** = HOCH$_2$CH$_2$CH(CH$_3$)COOH   and   **Q** = **R** = CH$_3$CH(OH)CH$_2$CH$_2$COOH

(C)   **P** = **S** = α-methyl-γ-butyrolactone   and   **Q** = **R** = γ-methyl-γ-butyrolactone

(D)   **P** = **R** = CH$_3$CH=CHCH$_2$COOH (E-isomer)   and   **Q** = **S** = CH$_3$CH(CN)CH=CH$_2$

Q.20   The major products **E** and **F** formed in the following reactions are

(A)   **E** = Br—(pyrrole)—Br   and   **F** = (pyridine with Br at 3-position)

(B)   **E** = (pyrrole)—Br   and   **F** = (pyridine with Br at 2-position)

(C)   **E** = Br,Br—(pyrrole)   and   **F** = (pyridine with Br at 4-position)

(D)   **E** = Br,Br,Br,Br—(pyrrole)   and   **F** = (N-Br pyridinium)
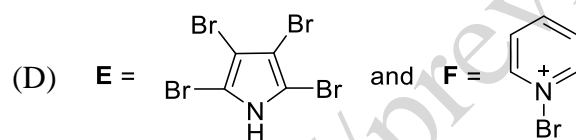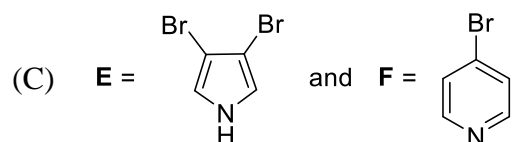
Q.21   The reaction that produces the following as a major product is

(A)   + $\xrightarrow{t\text{-BuOK}}$

(B)

1. BuLi
2.
3. PhCOCl
4. Na/Hg

(C) $\xrightarrow{\text{Lindlar's catalyst}}$
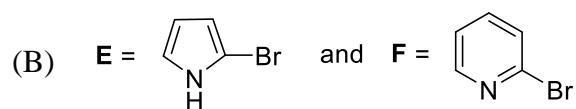
(D)

1. LiN(^{i}Pr)$_2$
2. (CH$_3$)$_2$S$_2$
3. NaIO$_4$
4. 110 °C
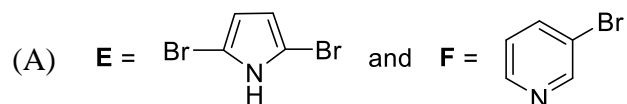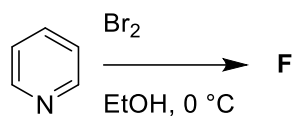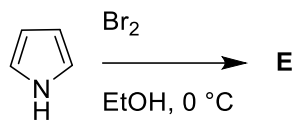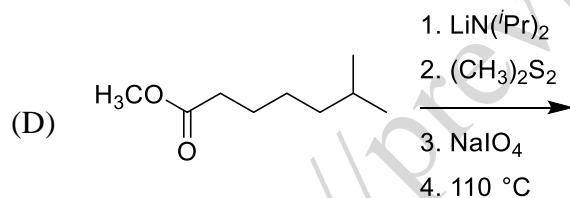
Q.22   The major product formed in the following reaction is

   $\xrightarrow[\text{2. H}_3\text{O}^+]{\text{1. NaBH}_4, \text{MeOH}}$

(A)   (B)

(C)   (D)
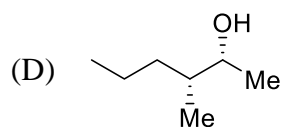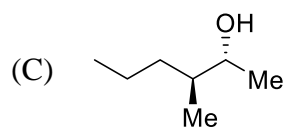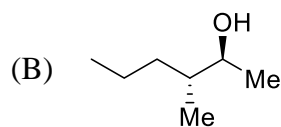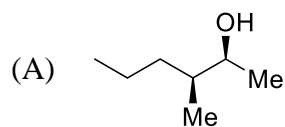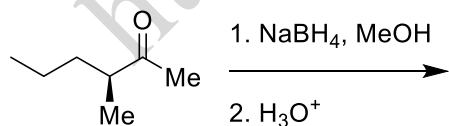
Q.23   The major product formed in the following reaction is

(A)

(B)

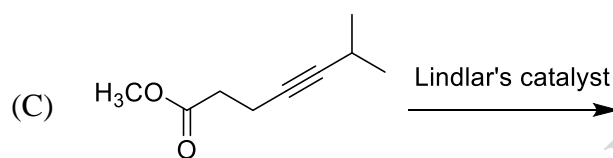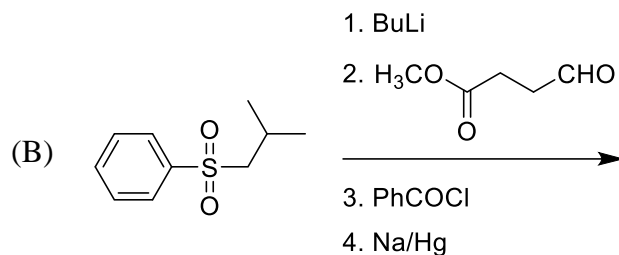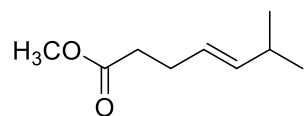(C)

(D)
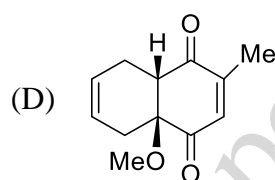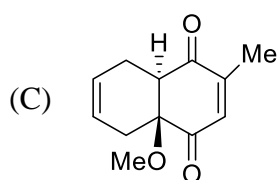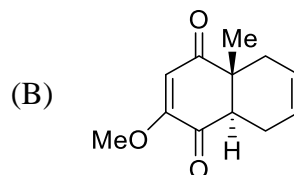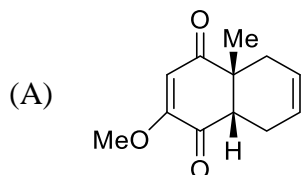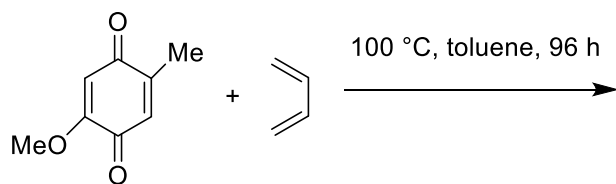
Q.24   In the following reaction, compound **Q** is

(A)

(B)

(C)

(D)
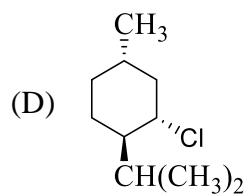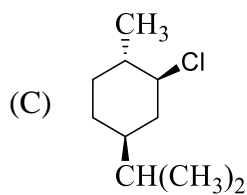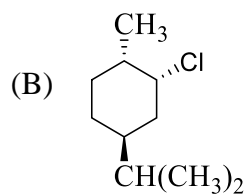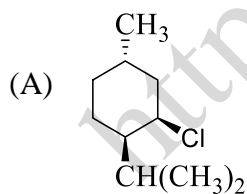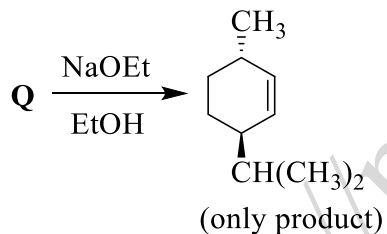
Q.25   Monochromatic X-rays having energy 2.8×10^{-15} J diffracted (first order) from (200) plane of a cubic crystal at an angle $8.5°$. The length of unit cell in Å of the crystal (*rounded off to one decimal place*) is
(*Given*: Planck's constant, $h = 6.626 \times 10^{-34}$ J s; $c = 3.0 \times 10^8$ m s^{-1})

(A) 2.4   (B) 3.4   (C) 4.8   (D) 9.8

Q.26   For $\alpha > 0$, the value of the integral $\int_{-\infty}^{+\infty} x e^{-\alpha x^2}\, dx$ is

(A) $\sqrt{\dfrac{\pi}{\alpha}}$ (B) ∞

(C) 0   (D) 1

Q.27   The volume correction factor for a non-ideal gas in terms of critical pressure (p_c), critical molar volume (V_c), critical temperature (T_c) and gas constant (R) is

(A) $\dfrac{RT_c}{8p_c}$ (B) $\dfrac{27R^2 T_c{}^2}{64p_c}$ (C) $\dfrac{8p_c V_c}{3T_c}$ (D) $3p_c V_c{}^2$

Q.28   Half-life $\left(t_{1/2}\right)$ of a chemical reaction varies with the initial concentration of reactant (A_o) as given below:

A_o (mol L^{-1})	5×10^{-2}	4×10^{-2}	3×10^{-2}
$t_{1/2}$ (s)	360	450	600

The order of the reaction is

(A) 0   (B) 1   (C) 2   (D) 3

Q.29   The CORRECT statement regarding the molecules BF$_3$ and CH$_4$ is

(A) Both BF$_3$ and CH$_4$ are microwave active

(B) Both BF$_3$ and CH$_4$ are infrared active

(C) CH$_4$ is microwave active and infrared inactive

(D) BF$_3$ is microwave active and infrared active

Q.30   For the consecutive reaction,

$$X \xrightarrow{ k_X } Y \xrightarrow{ k_Y } Z$$
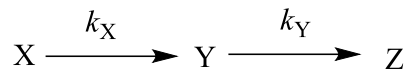
C_0 is the initial concentration of X. The concentrations of X, Y and Z at time t are C_X, C_Y and C_Z, respectively. The expression for the concentration of Y at time t is

(A) $\dfrac{k_X C_0}{k_Y - k_X} \left(e^{-k_X t} - e^{-k_Y t} \right)$

(B) $\dfrac{k_X C_X}{k_Y - k_X} \left(e^{-k_X t} - e^{-k_Y t} \right)$

(C) $\dfrac{k_X C_0}{k_Y - k_X} \left(e^{-k_Y t} - e^{-k_X t} \right)$

(D) $\dfrac{k_X C_X}{k_Y - k_X} \left(e^{-k_Y t} - e^{-k_X t} \right)$

SECTION - B

MULTIPLE SELECT QUESTIONS (MSQ)

Q. 31 – Q. 40 carry two marks each.

Q.31 The CORRECT statement(s) about the species is (are)

(A) $CpMo(CO)_3$ and $CpW(CO)_3$ are isoelectronic (where Cp is cyclopentadienyl)

(B) CH_2^- and NH_2 are isolobal and isoelectronic

(C) BH and CH are isolobal and isoelectronic

(D) CH_3 and $Mn(CO)_5$ are isolobal

Q.32 The complex(es) that show(s) Jahn-Teller distortion is (are)

(A) $[Co(CN)_5(H_2O)]^{3-}$ (B) $[NiF_6]^{2-}$

(C) $[Mn(CNMe)_6]^{2+}$ (D) $[Co(en)_2F_2]^+$

Q.33 The CORRECT statement(s) about sodium nitroprusside is (are)

(A) It is a paramagnetic complex

(B) Nitroprusside ion is formed in the brown ring test for nitrates

(C) It is used for the detection of S^{2-} in aqueous solution

(D) It contains nitrosyl ligand as NO^+

Q.34 The pigment responsible for red color in tomato has one functional group. The CORRECT statement(s) about this functional group is (are)

(A) It decolorizes bromine water

(B) It gives hydrazone derivative on reaction with 2,4-dinitrophenylhydrazine

(C) It gets cleaved on reaction with ozone

(D) It gives positive silver mirror test

Q.35   Hantzsch pyridine synthesis involves several steps. Some of those are

(A) Aldol reaction   (B) Darzens reaction

(C) Mannich reaction   (D) Michael addition

Q.36   The compound(s), which give(s) benzoic acid on oxidation with $KMnO_4$, is (are)

(A)   (B)

(C)   (D)
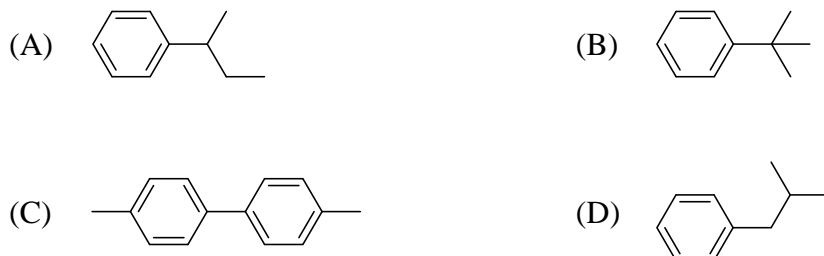
Q.37   The products **P** and **Q** formed in the reaction are

(A)

(B)

(C)

(D)
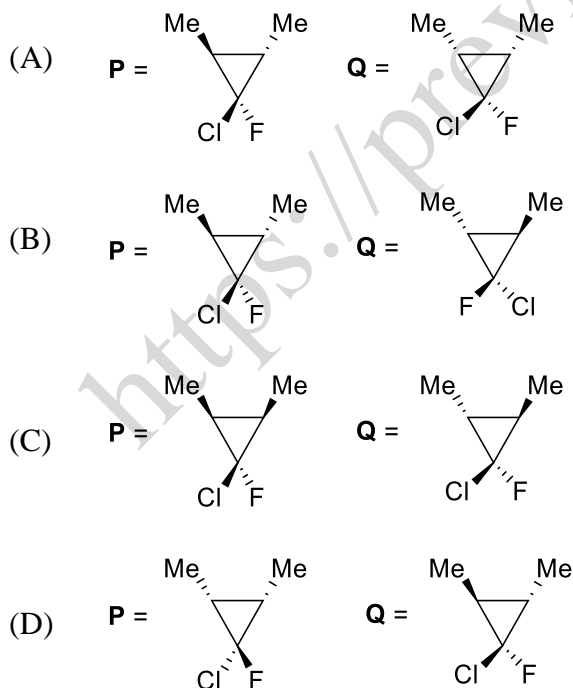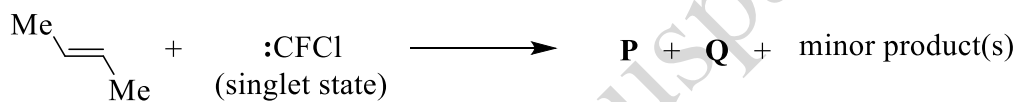
Q.38   The functional group(s) in reducing sugar that tests positive with Tollen's reagent is (are)

(A) Aldehyde   (B) Ketone

(C) Hemi-acetal   (D) Acetal

Q.39   Among the following, the anti-aromatic compound(s) is (are)

(A)   (B)

(C)   (D)

Q.40   The CORRECT Maxwell relation(s) derived from the fundamental equations of thermodynamics is (are)

(A) $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ (B) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

(C) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial p}{\partial S}\right)_V$ (D) $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

SECTION – C

NUMERICAL ANSWER TYPE (NAT)

Q. 41 – Q. 50 carry one mark each.

Q.41   The total number of optically active isomers of dichloridobis(glycinato)cobaltate(III) ion is _____.

Q.42   The total number of microstates possible for a d^8 electronic configuration is _____.

Q.43   For the following fusion reaction,
$$4\,^1H \longrightarrow \,^4He + 2\beta^+ + 2\upsilon + \gamma$$
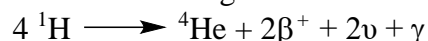the Q-value (energy of the reaction) in MeV (*rounded off to one decimal place*) is _____.
(*Given*: Mass of ^1H nucleus is 1.007825 u and mass of ^4He nucleus is 4.002604 u)

Q.44   MgO crystallizes as rock salt structure with unit cell length 2.12 Å. From electrostatic model, the calculated lattice energy in kJ mol^{-1} (*rounded off to the nearest integer*) is _____.
(*Given*: $N_A = 6.022 \times 10^{23}$ mol^{-1}; Madelung constant = 1.748;
$\varepsilon_0 = 8.854 \times 10^{-12}$ $J^{-1} C^2 m^{-1}$; charge of an electron = 1.602×10^{-19} C)

Q.45   Calcium crystallizes in *fcc* lattice of unit cell length 5.56 Å and density 1.4848 g cm^{-3}. The percentage of Schottky defects (*rounded off to one decimal place*) in the crystal is _____.
(*Given*: Atomic mass of Ca is 40 g mol^{-1}; $N_A = 6.022 \times 10^{23}$ mol^{-1})

Q.46   Among the following, the total number of terpenes(terpenoids) is _____.
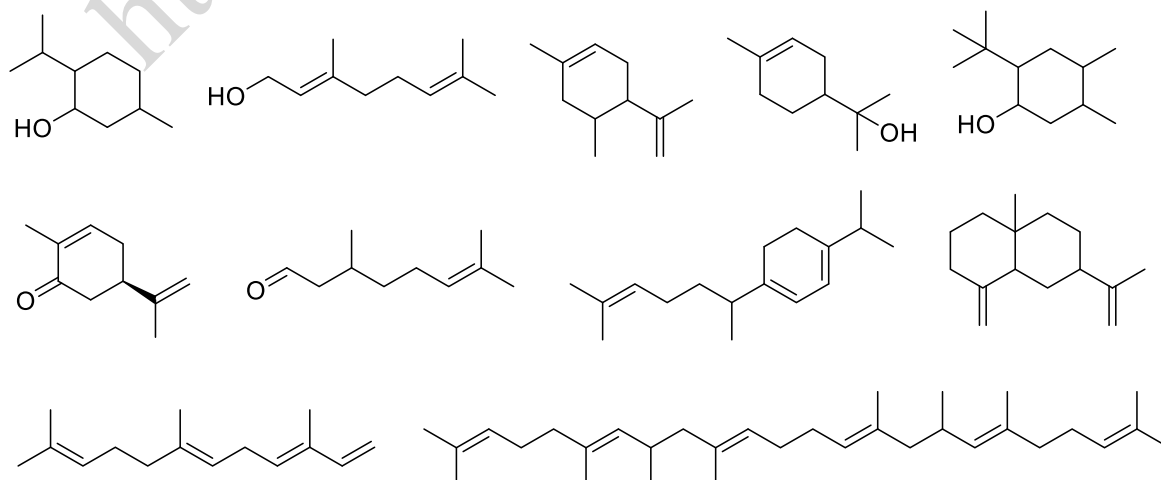
Q.47   A buffer solution is prepared by mixing 0.3 M NH_3 and 0.1 M NH_4NO_3. If K_b of NH_3 is 1.6×10^{-5} at 25 °C, then the pH (*rounded off to one decimal place*) of the buffer solution at 25 °C is _____.

Q.48   The dissociation constant of a weak monoprotic acid is 1.6×10^{-5} and its molar conductance at infinite dilution is 360.5×10^{-4} mho m^2 mol^{-1}. For 0.01 M solution of this acid, the specific conductance is $n \times 10^{-2}$ mho m^{-1}. The value of n (*rounded off to two decimal places*) is _____.

Q.49   Adsorption of a toxic gas on 1.0 g activated charcoal is 0.75 cm^3 both at 2.5 atm, 140 K and at 30.0 atm, 280 K. The isosteric enthalpy for adsorption of the gas in kJ mol^{-1} (*rounded off to two decimal places*) is _____.
(*Given*: $R = 8.314$ J K^{-1} mol^{-1})

Q.50   If the root mean square speed of hydrogen gas at a particular temperature is 1900 m s^{-1}, then the root mean square speed of nitrogen gas at the same temperature, in m s^{-1} (*rounded off to the nearest integer*), is _____.
(*Given*: atomic mass of H is 1 g mol^{-1}; atomic mass of N is 14 g mol^{-1})

Q. 51 – Q. 60 carry two marks each.

Q.51   If the crystal field splitting energy of $[Co(NH_3)_4]^{2+}$ is 5900 cm^{-1}, then the magnitude of its crystal field stabilization energy, in kJ mol^{-1} (*rounded off to one decimal place*), is _____.

Q.52   A salt mixture (1.0 g) contains 25 wt% of $MgSO_4$ and 75 wt% of M_2SO_4. Aqueous solution of this salt mixture on treating with excess $BaCl_2$ solution results in the precipitation of 1.49 g of $BaSO_4$. The atomic mass of **M** in g mol^{-1} (*rounded off to two decimal places*) is _____.
(*Given*: the atomic masses of Mg, S, O, Ba and Cl are 24.31, 32.06, 16.00, 137.33 and 35.45 g mol^{-1}, respectively)

Q.53   The intensity of a monochromatic visible light is reduced by 90% due to absorption on passing through a 5.0 mM solution of a compound. If the path length is 4 cm, then the molar extinction coefficient of the compound in M^{-1} cm^{-1} is _____.

Q.54   The surface tension (γ) of a solution, prepared by mixing 0.02 mol of an organic acid in 1 L of pure water, is represented as

$$\gamma^* - \gamma = A\log(1 + Bc)$$

γ^* is the surface tension of pure water, $A = 0.03$ N m^{-1}, $B = 50$ mol^{-1} L and c is concentration in mol L^{-1}. The excess concentration of the organic acid at the surface of the liquid, determined by Gibbs adsorption equation at 300 K is $n \times 10^{-6}$ mol m^{-2}. The value of n (*rounded off to two decimal places*) is _____.
(*Given*: $R = 8.314$ J K^{-1} mol^{-1})

Q.55   The separation of energy levels in the rotational spectrum of CO is 3.8626 cm^{-1}. The bond length (assume it does not change during rotation) of CO in Å (*rounded off to two decimal places*) is _____.
(*Given*: Planck's constant $h = 6.626 \times 10^{-34}$ J s; $N_A = 6.022 \times 10^{23}$ mol^{-1};
atomic mass of C is 12 g mol^{-1}; atomic mass of O is 16 g mol^{-1}; $c = 3 \times 10^8$ m s^{-1})

Q.56   A dilute solution prepared by dissolving a nonvolatile solute in one liter water shows a depression in freezing point of 0.186 K. This solute neither dissociates nor associates in water. The boiling point of the solution in K (*rounded off to three decimal places*) is _____.

(*Given*: For pure water, boiling point = 373.15 K;
cryoscopic constant = 1.86 K (mol kg^{-1})$^{-1}$; ebullioscopic constant = 0.51 K (mol kg^{-1})$^{-1}$)

Q.57   The thermodynamic data at 298 K for the decomposition reaction of limestone at equilibrium is given below

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

| Thermodynamic quantity	CaCO$_3$(s)	CaO(s)	CO$_2$(g)
μ° (kJ mol^{-1})	−1128.8	−604.0	−394.4
ΔH_f° (kJ mol^{-1})	−1206.9	−635.1	−393.5

The partial pressure of CO$_2$(g) in atm evolved on heating limestone (*rounded off to two decimal places*) at 1200 K is _____.
(*Given*: $R = 8.314$ J K^{-1} mol^{-1})

Q.58   The mean ionic activity coefficient of 0.004 molal CaCl$_2$ in water at 298 K (*rounded off to three decimal places*) is _____.
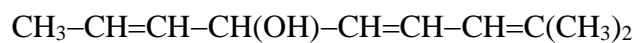(*Given*: Debye-Hückel constant for an aqueous solution at 298 K is 0.509 kg$^{1/2}$ mol$^{-1/2}$)

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Q.59   For the reaction,

$$Q + R \xrightleftharpoons[k_{-1}]{k_1} X \xrightarrow{k_2} P$$
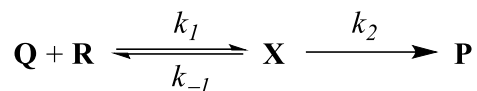
$k_1 = 2.5 \times 10^5$ L mol^{-1} s^{-1}, $k_{-1} = 1.0 \times 10^4$ s^{-1} and $k_2 = 10$ s^{-1}. Under steady state approximation, the rate constant for the overall reaction in L mol^{-1} s^{-1} (*rounded off to the nearest integer*) is _____.

Q.60   For the molecule,

CH$_3$−CH=CH−CH(OH)−CH=CH−CH=C(CH$_3$)$_2$

the number of all possible stereoisomers is _____.

END OF THE QUESTION PAPER

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