Roll No.				
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Signature of Invigilator

Question Booklet Series

X

PAPER-II

Question Booklet No.

Subject Code: 12

(Identical with OMR Answer Sheet Number)

CHEMICAL SCIENCES

Time: 2 Hours Maximum Marks: 200

Instructions for the Candidates

- 1. Write your Roll Number in the space provided on the top of this page as well as on the OMR Sheet provided.
- 2. At the commencement of the examination, the question booklet will be given to you. In the first 5 minutes, you are requested to open the booklet and verify it:
 - (i) To have access to the Question Booklet, tear off the paper seal on the edge of this cover page.
 - (ii) Faulty booklet, if detected, should be got replaced immediately by a correct booklet from the invigilator within the period of 5 (five) minutes. Afterwards, neither the Question Booklet will be replaced nor any extra time will be given.
 - (iii) Verify whether the Question Booklet No. is identical with OMR Answer Sheet No.; if not, the full set is to be replaced.
 - (iv) After this verification is over, the Question Booklet Series and Question Booklet Number should be entered on the OMR Sheet.
- 3. This paper consists of One hundred (100) multiple-choice type questions. All the questions are compulsory. Each question carries *two* marks.
- 4. Each Question has four alternative responses marked: (A) (B) (C) (D). You have to darken the circle as indicated below on the correct response against each question.

Example: (A) (B) (D), where (C) is the correct response.

- 5. Your responses to the questions are to be indicated correctly in the OMR Sheet. If you mark your response at any place other than in the circle in the OMR Sheet, it will not be evaluated.
- 6. Rough work is to be done at the end of this booklet.
- 7. If you write your Name, Phone Number or put any mark on any part of the OMR Sheet, except in the space allotted for the relevant entries, which may disclose your identity, or use abusive language or employ any other unfair means, such as change of response by scratching or using white fluid, you will render yourself liable to disqualification.
- 8. Do not tamper or fold the OMR Sheet in any way. If you do so, your OMR Sheet will not be evaluated.
- 9. You have to return the Original OMR Sheet to the invigilator at the end of the examination compulsorily and must not carry it with you outside the Examination Hall. You are, however, allowed to carry question booklet and duplicate copy of OMR Sheet after completion of examination.
- 10. Use only Black Ball point pen.
- 11. Use of any calculator, mobile phone, electronic devices/gadgets etc. is strictly prohibited.
- 12. There is no negative marks for incorrect answer.

21318 [Please Turn Over]

PAPER II

(CHEMICAL SCIENCES)

1. Considering anharmonicity, the pattern of the allowed vibrational energy levels may be given by:

$$\varepsilon_{v} = \left(v + \frac{1}{2}\right) \overline{\omega}_{e} - \left(v + \frac{1}{2}\right)^{2} \overline{\omega}_{e} x_{e} \text{ cm}^{-1} \left(v = 0, 1, 2, \ldots\right)$$

For a molecule with $\overline{\omega}_e = 4138.5 \, \mathrm{cm}^{-1}$ and $x_e = 0.0218$, the vibrational level of dissociation is

- (A) 45
- (B) 22
- (C) not determined, due to insufficient data
- (D) 90

- **2.** For a molecular potential energy curve the following is *not* correct:
 - (A) Born-Oppenheimer approximation is followed.
 - (B) The potential energy is of those electrons which are involved in bond-breaking and bond-making.
 - (C) It is specific for an electronic state.
 - (D) It may or may not have a minimum.

- **3.** For a variational optimization, the following is false:
 - (A) Wavefunction obtained and corresponding average energy are equally good.
 - (B) The energy is always upper bound to the true ground state energy.
 - (C) Energy optimized is correct upto first order in error of the wavefunction.
 - (D) The method is applicable to the first excited state, provided this is orthogonal to the ground state.

- **4.** According to the following treatment, a homonuclear diatomic is 50% covalent:
 - (A) VB treatment
 - (B) Generalized VB treatment
 - (C) LCAO-MO treatment
 - (D) LCAO-MO-configuration interaction treatment

- 5. Say, ΔE_v is the energy gap between two successive levels of a one-dimensional harmonic oscillator, ΔE_B is the energy gap between two successive levels of a quantum particle in a one-dimensional box of infinite height and wall. ΔE_n is taken as the energy gap between two successive levels of H-atom. For increasing quantum number which of the following is correct?
 - (A) ΔE_v remains same, ΔE_B increases and ΔE_n decreases.
 - (B) ΔE_v remains same, ΔE_B decreases and ΔE_n decreases.
 - (C) ΔE_v decreases, ΔE_B increases and ΔE_n increases.
 - (D) ΔE_v increases, ΔE_B increases and ΔE_n decreases.
- **6.** For an integral of the form $\int f_1 f_2 d\tau$ to exist, the functions f_1 and f_2 should be of the following type:
 - (A) One of f_1 and f_2 must belong to the totally symmetric representation.
 - (B) Functions f_1 and f_2 must belong to different irreducible representation.
 - (C) There is no restriction on the representations to which they can belong.
 - (D) Both f_1 and f_2 should belong to the same irreducible representation.

7. Information about initial pressure, initial volume, final volume and $\gamma \left(= \frac{C_P}{C_V} \right)$ are sufficient to calculate the final pressure of a sample of argon gas

calculate the final pressure of a sample of argon gas undergoing some process. The process of expansion involved is:

- (A) Adiabatic irreversible
- (B) Isothermal irreversible
- (C) Adiabatic reversible
- (D) Isothermal reversible
- **8.** Cooling effect in Joule–Thomson (JT) expansion of a gas corresponds to:
 - (A) μ_{JT} (JT coefficient) < 0 and Z (compressibility factor) > 1
 - (B) $\mu_{JT} < 0$ and Z < 1
 - (C) $\mu_{IT} > 0$ and Z > 1
 - (D) $\mu_{JT} > 0$ and Z < 1
 - **9.** Internal energy is independent of volume for:
 - (A) ideal gas only.
 - (B) a <u>gas</u> obeying equation of state P(V-b) = RT only.
 - (C) ideal gas as well as gas obeying equation of state $P(\overline{V} b) = RT$.
 - (D) ideal gas as well as gas obeying equation

of state
$$\left(P + \frac{a}{\overline{V}^2}\right)\overline{V} = RT$$
.

- 10. Depression in freezing point (ΔT_f) is related to concentration (m) as $\Delta T_f \propto m$, where:
 - (A) the solution is ideal solution and 'm' is molarity.
 - (B) the solution is ideal solution and 'm' is molality.
 - (C) the solution is ideally dilute solution and 'm' is molality.
 - (D) the solution is ideally dilute and 'm' is molarity.

- 11. Following (one) is purely an entropy effect:
 - (A) Lowering of vapour pressure of a solvent on addition of a non-volatile solute.
 - (B) Lowering of temperature of the system on dissolution of sugar in water.
 - (C) Spontaneous polymerization reaction.
 - (D) Obeyance of Henry's law by a solute in ideally dilute solution.
- **12.** A van der Waal gas behaves ideally at its Boyle temperature at a low pressure, due to the fact that:
 - (A) intermolecular attraction is negligible.
 - (B) repulsive and attractive parts of intermolecular interaction cancel each other, at Boyle temperature.
 - (C) as pressure tends to zero, compressibility factor (Z) tends to unity.
 - (D) intermolecular attraction and volume effect both are negligible.
- **13.** In the limit of high temperature, the molar vibrational energy relative to the zero point energy reduces to:
 - (A) zero
 - (B) R
 - (C) RT
 - (D) ∞
- 14. Two gaseous systems consist of mixture of atoms of type 'M' and 'N' in containers of equal volume for which the atomic partition functions are given as f_M and f_N , respectively. The first system consists of three atoms of 'M' and two atoms of 'N', while the second system contains three atoms of both types. What is the expression for total partition function of the system that would result in from mixing both systems in container of one of them?

(A)
$$\frac{f_M^3 \times f_N^2}{12}$$

- (B) $\frac{f_M^5 \times f_N^6}{30}$
- (C) $\frac{f_M^6 \times f_M^5}{144}$
- (D) $\frac{f_M^6 \times f_N^5}{86,400}$

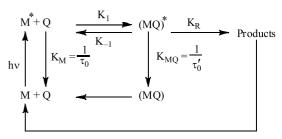
- **15.** A protein sample contains 50% of molecules of molecular weight 20,000; 40% of molecules of molecular weight 30,000 and 10% of molecules of molecular weight 60,000. What is the number average molecular weight of the protein sample?
 - (A) 28,000
 - (B) 32,857
 - (C) 37,142
 - (D) 2,80,000

- **16.** What is the ionic strength of a 1M solution of Na_3PO_4 ?
 - (A) 1M
 - (B) 3M
 - (C) 6M
 - (D) 12M

- 17. Packing fraction of hcp structure is:
 - (A) 0.86
 - (B) 0.34
 - (C) 0.74
 - (D) 0.68

- **18.** In the ground state of an atom, orbital energies of core level and next two subsequent higher levels are respectively. ε_x , ε_y and ε_z . The Auger process involving one electron in each of these orbitals is associated with E_{Auger} roughly as:
 - (A) ε_{x}
 - (B) $\varepsilon_x \varepsilon_v \varepsilon_z$
 - (C) $\varepsilon_x \varepsilon_y + \varepsilon_z$
 - (D) $\varepsilon_x \varepsilon_z + \varepsilon_y$

19. Consider the following photochemical scheme:



Which of the following statements is correct considering the above mentioned photochemical scheme?

- (A) If $K_R \gg K_1[Q]$, then the reaction is diffusion-limited.
- (B) If $K_R >> K_1$ [Q], the equilibrium is reached prior to the formation of products.
- (C) If $\tau_0 = \tau_0'$, then MQ is an exciplex.
- (D) The reaction between M and Q is controlled by both static and dynamic quenching process.

20. The rate expression for decomposition of acetaldehyde may be represented as follows:

$$Rate = K_2 \left(\frac{K_1}{K_3}\right)^{1/2} \cdot C_{acetaldehyde}^{3/2}$$

where $C_{acetaldehyde}$ denotes the concentration of acetaldehyde. If the activation energies involved in various steps of the above mentioned reaction are E_1 , E_2 and E_3 , then the overall activation energy (E) is given as:

(A)
$$E = \frac{1}{2} (E_2 + E_1 - E_3)$$

(B)
$$E = \frac{1}{2} (E_2 + E_1 - 2E_3)$$

(C)
$$E = \frac{1}{2} (E_2 + 2E_1 - E_3)$$

(D)
$$E = \frac{1}{2} (2E_2 + E_1 - E_3)$$

21. Which one is correct among the following?

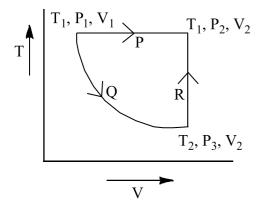
(A)
$$\overline{S_i} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\left\{n_{j\neq i}\right\}}$$

(B)
$$\overline{H_i} = -\left(\frac{\partial H}{\partial n_i}\right)_{T,P,\left\{n_{j\neq i}\right\}}$$

(C)
$$\mu_i = -\left(\frac{\partial U}{\partial n_i}\right)_{S,V\left\{n_{j\neq i}\right\}}$$

(D)
$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\left\{n_{j\neq i}\right\}} = -\left(\frac{\partial A}{\partial n_i}\right)_{T,V,\left\{n_{j\neq i}\right\}}$$

22. Define the correct path as marked in 'P', 'Q' and 'R' in following diagram:



- (A) P: Reversible, Isothermal;
 - Q: Reversible, Adiabatic;
 - R: Irreversible, Constant volume.
- (B) P: Irreversible, Isothermal;
 - Q: Reversible, Non-adiabatic;
 - R: Reversible, Constant volume.
- (C) P: Reversible, Isothermal;
 - Q: Reversible, Adiabatic;
 - R: Reversible, Constant volume.
- $(D)\ \ P: Irreversible, \ Is othermal;$
 - Q: Irreversible, Adiabatic;
 - R: Irreversible, Constant volume.

23. Match *Column P* with *Column Q*:

Column P

Column O

- (a) CdS/ZnS
- (i) Domination of $S_0 \leftarrow S_2$ fluorescence
- (b) Py C₆₀
- (ii) Appearance of two numbers of Soret Bands
- (c) Azulene
- (iii) Exhibition of triple exponential decay

(d)

- (d) Bisporphyrin (iv) Generation of triplet state upon irradiation by laser pulse of suitable wavelength
 - (a) (b) (c)
 - (A) (i) (ii) (iii) (iv)
 - (B) (ii) (iii) (iv) (i)
 - (C) (iv) (iii) (ii) (i)
 - (D) (iii) (iv) (i) (ii)

24. Consider the transition state formulation of the specific rate of a simple bimolecular reaction,

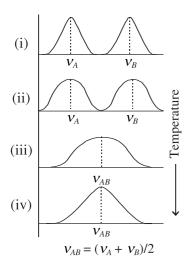
$$A + B \xrightarrow{k_1} [AB^{\neq}] \xrightarrow{k_2} Product,$$

where the activated complex $[AB^{\neq}]$ establishes fast equilibrium with reactants. If activation energy is achieved by collisions, k_{-1} should be equal to: $(Z \text{ and } Z' \text{ are the frequency of collisions for the forward and reverse step, respectively)$

(A)
$$Z'e^{-E^{\neq}/RT}$$

- (B) $Z'e^{E^{\neq}/RT}$
- (C) $Ze^{-E^{\neq}/RT}$
- (D) Z'

25. In a NMR experiment, two ¹H at two different environments exchange rapidly and the rate of exchange increase with temperature from (i) \rightarrow (iv). The 1st order rate coefficient $k_a \left(\approx \frac{1}{\tau} \right)$ for the exchange process can be determined directly from the figure $\left(\tau = \frac{1}{v_A - v_B} \right)$ under the temperature condition shown in:



- (A) (i)
- (B) (ii)
- (C) (iii)
- (D) (iv)

26. NH₃ molecule belongs to C_{3V} point group, the character table of which is given below:

C_{3V}	Е	$2C_3$	$3\sigma_{_{ m V}}$	
A_1	1	1	1	Z
A_2	1	1	-1	R_{Z}
E	2	-1	0	$(x, y) (R_x, R_y)$

 $C_3(Z)$ and $\sigma(xz)$ matrices are $\begin{pmatrix} -\frac{1}{2} & \sqrt{3}/2 \\ -\sqrt{3}/2 & -\frac{1}{2} \end{pmatrix}$ and

 $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ respectively [considering transformation in x and y coordinates only]. If σ'_{v} and σ''_{v} make 120° and 240° angles with , $\sigma_{v}(xz)$, the matrices are:

(A)
$$\begin{pmatrix} \frac{-1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$
 and
$$\begin{pmatrix} \frac{-1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

(B)
$$\begin{pmatrix} \frac{-1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$$
 and
$$\begin{pmatrix} \frac{-1}{2} & \frac{\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$$

(C)
$$\begin{pmatrix} \frac{\sqrt{3}}{2} & \frac{-1}{2} \\ \frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix}$$
 and $\begin{pmatrix} \frac{-1}{2} & \frac{\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$

(D)
$$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$
 and
$$\begin{pmatrix} \frac{-1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$$

- X-8
- **27.** Creatine phosphate is hydrolysed spontaneously to form creatine and phosphoric acid ($\Delta G^{\circ} = -43.5 \text{ kJ} \text{ mole}^{-1}$), while ATP is hydrolysed to form ADP and phosphoric acid ($\Delta G^{\circ} = -39.7 \text{ kJ mole}^{-1}$). An enzyme couples these reactions to produce ATP from ADP by a reaction whose logarithm of equilibrium constant at 27°C is:
 - (A) 14·5
 - (B) 0.33
 - (C) 7·25
 - (D) 0.66
- **28.** Potential energy (V) of vibration of a polyatomic molecule is given by

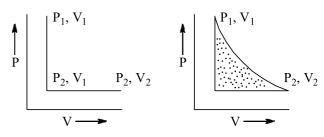
$$V = \frac{1}{2} \sum_{ij} b_{ij} q_i q_j$$
, where q_i, q_j are displacement

coordinates of the atoms. Identify the correct force constant (b_{ij}) [suffix 'o' means around minimum of potential energy]

(A)
$$\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_{q}$$

- (B) $\left(\frac{\partial V}{\partial q_i}\right)_{\alpha}$
- (C) $\left(\frac{\partial V}{\partial q_j}\right)_{i=1}^{\infty}$
- (D) $\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)$
- **29.** Number of independent electronic wavefunctions corresponding to each of the following diatomic-molecule terms: $^1\Sigma^-$, $^3\Sigma^+$, $^3\Pi$, are respectively as:
 - (A) 1, 1, 2
 - (B) 1, 3, 6
 - (C) 2, 3, 2
 - (D) 1, 3, 2

30. An ideal gas expands isothermally from P_1 , V_1 to P_2 , V_2 by both irreversible (at constant P_2) and reversible paths to give following P–V plots respectively.



The area under the dotted part is equal to:

- (A) irreversible work
- (B) reversible work
- (C) overall work
- (D) difference between reversible and irreversible works

31. The Butler-Volmer relation,

 $I = I_o \ [e^{\alpha F \omega / RT} - e^{-(1-\alpha)F \omega / RT}], \text{ shows, on expanding exponential terms, that for small polarization:}$

- (A) cathod potential is a linear function of logarithm of current density.
- (B) cathod potential is a linear function of current density.
- (C) cathod potential is invariant of current density.
- (D) cathod potential is invariant of current density for small polarization but varies linearly for high polarization.

- **32.** If a molecule contains an S_n axis of odd order, the molecule must contains independently:
 - (A) a C_n axis collinear with the S_n axis.
 - (B) a σ plane perpendicular to C_n axis.
 - (C) both C_n axis collinear with S_n axis and σ plane perpendicular to C_n axis.
 - (D) a center of symmetry (i).

33. The character table of D_{3h} point group is given:

\mathbf{D}_{3h}	Е	$2C_3$	$3C_2$	$\boldsymbol{\sigma}_{\!_{h}}$	$2S_3$	$3\sigma_{v}$	
Γ_1	1	1	1	1	1	1	
Γ_2	1	1	-1	1	1	-1	R_z
Γ_3	2	-1	0	2	-1	0	(x, y)
Γ_4	1	1	1	-1	-1	-1	
Γ_5	1	1	-1	-1	-1	1	z
Γ_6	2	-1	0	-2	1	0	R_{z} (x, y) z (R_{x}, R_{y})

Identify A_2' and E'' among the irreducible representation denoted by $\Gamma's$

- (A) Γ_1 and Γ_2 respectively
- (B) Γ_2 and Γ_3 respectively
- (C) Γ_2 and Γ_6 respectively
- (D) Γ_4 and Γ_6 respectively
- **34.** In an enzyme inhibition reaction, the slopes of the Lineweaver–Burk plots are found to vary linearly with the drug concentration. The mechanism of inhibition follows:
 - (A) Competitive inhibition at low drug concentration but non-competitive inhibition at high drug concentration
 - (B) Non competitive inhibition
 - (C) Uncompetitive inhibition
 - (D) Competitive inhibition
 - **35.** The major product of the following reaction is:

36. Indicate the major product of the following reaction.

37. The major product of the following photochemical reaction is:

$$(C) \qquad O \qquad (D) \qquad \bigcup_{i=1}^{N} H$$

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12-II

X-10

38. Predict the major product of the given reaction:

$$(A) \qquad (B) \qquad (B) \qquad (C) \qquad (B) \qquad (B) \qquad (C) \qquad (C) \qquad (C) \qquad (D) \qquad (B) \qquad (B) \qquad (C) \qquad (C)$$

39. The major products X and Y in the following reaction sequence are:

$$Mg/65^{\circ}C \longrightarrow X \xrightarrow{CO_2/H_3O^+} Y$$

$$(A) \quad X = \bigvee_{MgCl} Y = \bigvee_{H} CO_2H$$

$$(B) \quad X = \bigvee_{MgCl} Y = \bigvee_{H} CO_2H$$

$$(C) \quad X = \bigvee_{MgCl} Y = \bigvee_{MgCl} CO_2H$$

$$(D) \quad X = \bigvee_{MgCl} Y = \bigvee_{MgCl} CO_2H$$

40. The correct product of the following reaction is:

41. Indicate the major product of the following given reaction.

42. The major product of the following photochemical reaction is:

43. The major product of the following reaction is:

$$\begin{array}{c}
O \\
\hline
Br
\end{array}$$

$$\begin{array}{c}
KO^{t}Bu \\
\hline
^{t}BuOH/\Delta
\end{array}$$

$$(C) \qquad (D) \qquad (D)$$

44. The point group of the following compound is:

- (A) D_{3h}
- (B) C_{3h}
- (C) C_3
- (D) C_{3v}

45. The product of following concerted reaction is formed through:

- (A) 4π -disrotatory electrocyclisation
- (B) 6π -disrotatory electrocyclisation
- (C) 6π -conrotatory electrocyclisation
- (D) 4π -conrotatory electrocyclisation

46. The major product of the following reaction is:

47. An organic compound with molecular formula $C_7H_{12}O_2$ exhibits the following data in 1H NMR spectrum. δ 7·10 (1H, dt, $J_1 = 16Hz$, $J_2 = 7\cdot2Hz$), 5·89 (1H, dt, $J_1 = 16Hz$, $J_2 = 2Hz$), 4·10 (2H, q, $J_2 = 7\cdot2Hz$), 2·10 (2H, m), 1·25 (3H, t, $J_2 = 7\cdot2Hz$), 0·90 (3H, t, $J_2 = 7\cdot2Hz$) ppm.

The correct structure of the compound among the choices given below is:

48. The major product of the following reaction is:

Br
$$CO_{2}H$$

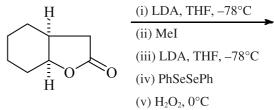
$$(A)$$

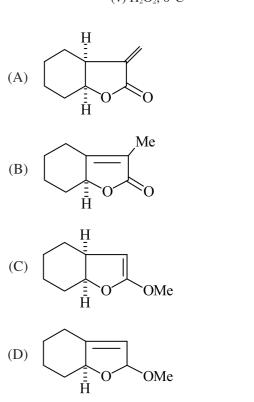
$$CO_{2}H$$

$$(B)$$

$$CO_{2}H$$

49. The major product of the following reaction is:





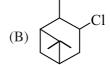
50. Increasing reactivity of the following dienes towards tetracyanoethylene as dienophile in the Diels-Alder reaction is:

- (A) III < II < I
- (B) II < I < III
- (C) II < III < I
- (D) III < I < II

51. The major product of the following reaction is:



(A) C

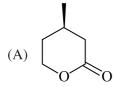


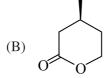
(C) Cl

(D)

52. The product of the reaction is:

HOOC
$$CO_2Me$$
 $1. B_2H_6$ $2. H^+, heat$



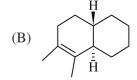




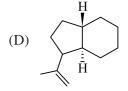
53. The major product of the reaction is:

$$HO$$
 $\stackrel{\stackrel{\circ}{\longrightarrow}}{\stackrel{\circ}{\longrightarrow}}$

 $(A) \quad \begin{array}{c} H \\ \vdots \\ \ddot{H} \end{array}$



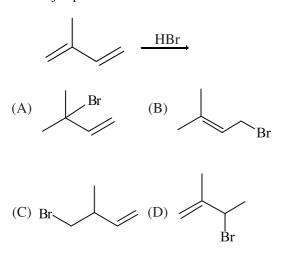
 $(C) \qquad \begin{array}{c} H \\ \vdots \\ H \end{array}$



54. The major product of the reaction is:

$$(A) \qquad \begin{matrix} H & O \\ \vdots & \vdots \\ O & \vdots \\ H \end{matrix}$$

55. The major product of the reaction is:



56. The product [Y] of the following reaction sequence is:

$$(A) O (C) O (C) O (C)$$

$$(B) O (C) O (C) O (C) O (C)$$

$$(B) O (C) O (C) O (C) O (C)$$

$$(C) O (C) O (C) O (C)$$

$$(C) O (C) O (C) O (C)$$

$$(C) O (C) O (C)$$

$$(C) O (C) O (C)$$

$$(C) O (C) O (C)$$

(D)

57. The product [Y] of the following reaction sequence is:

$$OMe$$

$$Me_3SiC1$$

$$Et_3N$$

$$[X]$$

$$[Y]$$

$$(A) \quad Me_3SiO \xrightarrow{\stackrel{\bullet}{\overline{H}}} CO_2Me$$

$$(B) \begin{picture}(60,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0)$$

$$(C) \qquad \underbrace{\begin{array}{c} OMe \\ H \\ \vdots \\ Me_3SiO \end{array}}_{CO_2Me}$$

$$(D) \qquad \underbrace{ \begin{array}{c} OMe \\ \vdots \\ H \\ \vdots \\ CO_2Me \end{array} }$$

$$\begin{array}{c} O \\ + CH_2 = C = O \end{array} \xrightarrow{ZnCl_2} \begin{array}{c} Cl_2 \\ \hline 20^{\circ}C \end{array}$$

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59. The product of the reaction is:

$$\begin{array}{c} & \\ \hline \\ N \\ \hline \\ \hline \\ 2. \text{ H}^{\oplus}, \text{ heat} \\ \end{array}$$

$$(A) \begin{picture}(60,0) \put(0,0){\line(1,0){10}} \put$$

$$(B) \begin{picture}(60,0) \put(0,0){\ovalpha} \put(0,0){\oval$$

$$(D) \qquad \qquad \underset{HO}{\longleftarrow} N$$

60. The major product of the reaction is:

61. The product of the following reaction is:

$$(A)$$

$$(B)$$

$$(C)$$

$$(D)$$

$$(D)$$

$$(D)$$

$$(A)$$

$$(A)$$

$$(A)$$

$$(A)$$

$$(A)$$

$$(A)$$

$$(A)$$

$$(A)$$

$$(B)$$

$$(C)$$

$$(C)$$

$$(C)$$

$$(D)$$

$$(D)$$

$$(D)$$

$$(D)$$

$$(D)$$

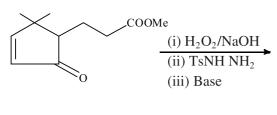
$$(D)$$

$$(D)$$

$$(D)$$

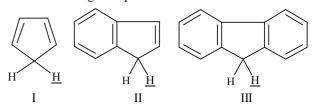
[Please Turn Over]

62. The major outcome of the following reaction is:



63. The outcome of the reaction sequence is:

64. Increasing order of the acidity of the marked 'H' of the following compounds is:



- (A) III < II < I
- (B) II < I < III
- (C) I < III < II
- (D) I < II < III

65. Salicylic acid with acetic anhydride in the presence of a catalytic amount of H_2SO_4 produces:

66. An organic compound $(C_7H_{14}O_2)$ exhibited the following spectral data:

IR: 1740 cm⁻¹

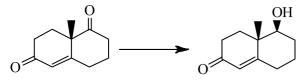
¹H NMR : δ 4·1 (m, 1H), 2·2 (t, 2H), 1·6 (m, 2H), 1·2 (d, 6H), 0·9 (t, 3H) ppm

The structure of the compound is

(C) CH₃-CH-C-O-CH-CH₃ O CH

(D) CH₃-CH₂-CH₂-C-O-CH-CH₃

67. The most suitable reagent for the following conversion is:



- (A) LiBH₄ in THF
- (B) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, EtOH
- (C) $Zn(BH_4)_2$, DME
- (D) LiAlH(OEt)₃, THF
- **68.** The toxicity of CN^- is due to the fact that:
 - (A) it stabilises Fe(II) and Cu(II) but regeneration of Fe(III) and Cu(I) is not possible.
 - (B) it stabilises Fe(III) and Cu(II) and blocks the cytochrome C.
 - (C) it blocks the cytochrome C oxidase involved in the respiratory chain by stabilising Fe(III) and Cu(I).
 - (D) it replace oxygen from sixth coordination site of haemoglobin and myoglobin.

- **69.** The equatorial \widehat{FSF} bond angles in SF_4 and SOF_4 are:
 - (A) 120° and 120°, respectively.
 - (B) 101° and 115°, respectively.
 - (C) 115° and 101°, respectively.
 - (D) 115° and 115°, respectively.
- **70.** The correct set of statements amongst the following on the ¹⁹F NMR study of PF₅ molecule is:
 - (i) one broad peak at room temperature.
 - (ii) two peaks at -80°C.
 - (iii) two peaks at room temperature.
 - (iv) one broad peak at -80°C.
 - (A) (i) and (ii)
 - (B) (ii) and (iii)
 - (C) (iii) and (iv)
 - (D) (ii) and (iv)
- **71.** The correct order of LMCT energies in the following species is:
 - (A) $MnO_4^- < CrO_4^{2-} < VO_4^{3-}$
 - (B) $MnO_4^- > CrO_4^{2-} > VO_4^{3-}$
 - (C) $MnO_4^- > CrO_4^{2-} < VO_4^{3-}$
 - (D) $MnO_4^- < CrO_4^{2-} > VO_4^{3-}$
 - **72.** Kaolin is an example of:
 - (A) pyrosilicates
 - (B) chain silicates
 - (C) sheet silicates
 - (D) cyclic silicates
- **73.** The standard potential for the reduction of ClO_4^- to Cl_2 is:
 - (A) 1.624 V
 - (B) 2·436 V
 - (C) 1·392 V
 - (D) 3·248 V

Given: ClO_4^-/ClO_3^- ; $E^\circ = 1.201V$ ClO_3^-/ClO_2^- ; $E^\circ = 1.181V$ ClO_2^-/ClO^- ; $E^\circ = 1.678V$ ClO^-/Cl_2 ; $E^\circ = 1.630V$ 12-II X-18

- **74.** B_2H_6 reacts with NH_3 forming a compound B_2H_6 :2 NH_3 . The resulting compound:
 - (A) is ionic and exists as $[BH_2(NH_3)_2]^+$ and BH_4^- ions.
 - (B) is converted into inorganic benzene on heating.
 - (C) Statement (A) is correct but (B) is incorrect.
 - (D) Both (A) and (B) are correct.
- **75.** In $[Mo_2(S_2)_6]^{2-}$ cluster, the number of bridging S_2^{2-} and coordination number of Mo respectively are:
 - (A) 2 and 8
 - (B) 2 and 6
 - (C) 1 and 8
 - (D) 4 and 8

- **76.** In acid solution, $[Co(NH_3)_5CO_3]^+$ is converted to aqua complex with the release of CO_2 . If the reaction is carried out in $H_2^{18}O$, do you expect the presence of ¹⁸O in the resulting complex?
 - (A) Yes, as water adds with $[Co(NH_3)_5]^{3+}$.
 - (B) No, as the substitution occurs without breaking metal-ligand bond.
 - (C) Yes, as exchange of H₂¹⁸O with H₂O occurs in the product.
 - (D) No, as H_2O attacks the intermediate at a faster rate than $H_2^{18}O$.

- 77. The compounds of Xe which possess same shapes as SO_4^{2-} and SF_4 respectively are:
 - (A) XeF₄ and XeO₄
 - (B) XeO₄ and XeO₂F₂
 - (C) XeO₄ and XeF₄
 - (D) XeF₄ and XeO₂F₂

- **78.** Identify the correct set of statements from the following on ferrimagnetism, observed in the magnetite which exhibits:
 - (i) Fe(II) and Fe(III) in the octahedral structure
 - (ii) Fe(II) and Fe(III) in the tetrahedral structure
 - (iii) Fe(II) in the tetrahedral structure
 - (iv) Fe(III) in the tetrahedral structure
 - (A) (i) and (iii)
 - (B) (i) and (iv)
 - (C) (i) and (ii)
 - (D) (ii) and (iii)
- **79.** The compound, among the following, having P–P single bond is:
 - $(A) P_4O_6$
 - (B) P_4O_{10}
 - (C) $H_4P_2O_7$
 - (D) $H_4P_2O_6$
- **80.** The X-ray powder pattern of NaCl exhibits an intense peak at $2\theta = 31.74^{\circ}$ using X-rays of wavelength of 1.54×10^{-8} cm. The spacing between the planes of NaCl crystal is:
 - (A) 5.63Å
 - (B) 1·48Å
 - (C) 2.82Å
 - (D) 4·23Å
- **81.** Among the following, identify the correct set of statements for Polarography:
 - (i) The dropping mercury electrode is the cathode
 - (ii) $E_{1/2}$ is nearly equal to E° of analyte.
 - (iii) Supporting electrolyte is added to the solution in order to increase the Faradaic current.
 - (iv) $E_{1/2}$ of analyte changes on addition of a reagent which forms complex with the analyte.
 - (A) (i), (ii) and (iv)
 - (B) (i), (ii) and (iii)
 - (C) Only (i) and (iv)
 - (D) Only (iii)

- **82.** 200 mL of a sample water contains 0.006 g CaCO₃ salt. The hardness of this water is:
 - (A) 20 ppm
 - (B) 15 ppm
 - (C) 40 ppm
 - (D) 30 ppm
- **83.** The analysis of phosphorous content of a 'Cola' drink involves:
 - (A) oxidation of a Co(II) salt
 - (B) reduction of a Mn(VII) salt
 - (C) reduction of a Mo(VI) salt
 - (D) oxidation of a Cu(II) salt
- **84.** The tanning of leather industry uses the coordination complex of the metal:
 - (A) W
 - (B) Mo
 - (C) Cr
 - (D) Mn
- **85.** 0.4506 gm of an iron ore is converted to Fe₂O₃ after a series of chemical treatments. If the weight of the obtained Fe₂O₃ is 0.2113 gm, the percentage of iron (atomic weight of iron = 55.85 g/mol) in the given ore is:
 - (A) 11·79%
 - (B) 21·70%
 - (C) 6.86%
 - (D) 32·80%
- **86.** The *styx* codes of B_2H_6 and B_4H_{10} , respectively are:
 - (A) 2002 and 4012
 - (B) 3103 and 2102
 - (C) 4120 and 2012
 - (D) 4012 and 2002

- **87.** The unit cells of 'wurtzite' and 'rutile' respectively are:
 - (A) cubic and rhombohedral
 - (B) hexagonal and tetragonal
 - (C) tetragonal and cubic
 - (D) rhombohedral and hexagonal
- **88.** The point groups of [PtCl₄]²⁻ and BeF₂, respectively are:
 - (A) C_{4v} and $C_{\infty v}$
 - (B) C_{2v} and C_{2h}
 - (C) D_{4d} and $D_{\infty v}$
 - (D) D_{4h} and $D_{\infty h}$
- **89.** The potential of the H^+/H_2 couple of pH 7·0 can be calculated to be:
 - (A) -0.059V
 - (B) -0.82V
 - (C) -0.21V
 - (D) -0.41V
- **90.** The volume of 2N Na₂EDTA solution required to reach the end-point in a complexometric titration of an aqueous solution of 50 gm CaCO₃ is:
 - (A) 50 mL
 - (B) 1000 mL
 - (C) 500 mL
 - (D) 2000 mL
- **91.** The spin multiplicity of Carbon (${}_{6}C^{12}$) atom in ground state is:
 - (A) 2
 - (B) 3
 - (C) 1
 - (D) 4

- **92.** Which of the following species doesn't exist?
 - (A) PbI₄
 - (B) PbCl₄
 - (C) PbI₂
 - (D) PbCl₂
- **93.** Which one of the following compounds shows both geometrical isomerism and optical isomerism?
 - (A) $[Co(en)_3]Cl_3$
 - (B) $[Co(NH_3)_3Cl_3]$
 - (C) $[Co(en)_2Cl_2]Cl$
 - (D) $[Co(NH_3)_5Cl]Cl_2$
- **94.** Na₂S upon treatment with sodium nitroprusside solution forms a purple solution due to the formation of:
 - (A) $Na_4[Fe(CN)_6]$
 - (B) Na₃[Fe(CN)₅NOS]
 - (C) Na₄[Fe(CN)₅NOS]
 - (D) Na₂[Fe(CN)₅NOS]
- **95.** In which of the following transformations, the state of hybridisation of the central atom does not change?
 - (A) $BF_3 \rightarrow BF_4^-$
 - (B) $NH_3 \rightarrow NH_4$
 - (C) $CO_2 \rightarrow HCO_2H$
 - (D) $PF_3 \rightarrow PF_5$
- **96.** The correct order of energy required to remove the highest energy electron from the following species is:
 - $(A) N > N_2 > NO$
 - (B) $N_2 > N > NO$
 - (C) $NO > N > N_2$
 - (D) $N_2 > NO > N$

- **97.** The pH of a 60% ionized 0.01 N acid solution is:
 - (A) 1·44
 - (B) 0·44
 - (C) 2·22
 - (D) 4·44

- **98.** The correct order of lattice energy of the fluorides of Cr^{2+} , Mn^{2+} and Ni^{2+} is:
 - (A) $Ni^{2+} > Mn^{2+} > Cr^{2+}$
 - (B) $Ni^{2+} > Cr^{2+} > Mn^{2+}$
 - (C) $Cr^{2+} > Ni^{2+} > Mn^{2+}$
 - (D) $Cr^{2+} > Mn^{2+} > Ni^{2+}$

- **99.** The cluster type and geometry of the species $[Rh_0P(CO)_{21}]^{2-}$ are:
 - (A) Closo, tricapped trigonal prism
 - (B) Arachno, trigonal prism
 - (C) Nido, capped square antiprism
 - (D) Nido, bicapped trigonal prism

- **100.** Amongst the following identify the correct set of statements for complexes of lanthanide ions.
 - (i) Metal-ligand bond is significantly ionic.
 - (ii) Complexes rarely show isomerism.
 - (iii) Coordination number is not more than 8.
 - (iv) The magnetic moments are not accounted for even approximately by spin only value.
 - (A) (i) and (ii)
 - (B) (i), (ii) and (iii)
 - (C) (ii) and (iv)
 - (D) (i), (ii) and (iv)

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Space for Rough Work

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Space for Rough Work