

13**WRITTEN TEST****Test Booklet No.****CHEMISTRY**

Name of Applicant Answer Sheet No.

Application ID : Signature of Applicant :

Date of Examination: Signature of the Invigilator(s)

1.

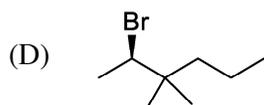
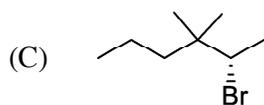
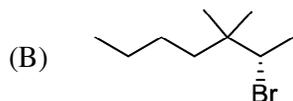
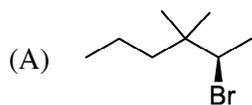
Time of Examination : 2.

Duration : 1 Hour]**[Maximum Marks : 50****IMPORTANT INSTRUCTIONS**

- (i) The question paper is in the form of Test-Booklet containing **50 (Fifty)** questions. All questions are compulsory. Each question carries four answers marked (A), (B), (C) and (D), out of which only one is correct.
- (ii) On receipt of the Test-Booklet (Question Paper), the candidate should immediately check it and ensure that it contains all the pages, i.e., **50** questions. Discrepancy, if any, should be reported by the candidate to the invigilator immediately after receiving the Test-Booklet.
- (iii) A separate Answer-Sheet is provided with the Test-Booklet/Question Paper. On this sheet there are **50** rows containing four circles each. One row pertains to one question.
- (iv) The candidate should write his/her Application number at the places provided on the cover page of the Test-Booklet/Question Paper and on the Answer-Sheet and **NOWHERE ELSE**.
- (v) No second Test-Booklet/Question Paper and Answer-Sheet will be given to a candidate. The candidates are advised to be careful in handling it and writing the answer on the Answer-Sheet.
- (vi) For every correct answer of the question **One (1) mark will be awarded**. For every unattempted question, Zero (0) mark shall be awarded. **There is no Negative Marking**.
- (vii) Marking shall be done only on the basis of answers responded on the Answer-Sheet.
- (viii) To mark the answer on the Answer-Sheet, candidate should **darken** the appropriate circle in the row of each question with Blue or Black pen.
- (ix) For each question only **one** circle should be **darkened** as a mark of the answer adopted by the candidate. If more than one circle for the question are found darkened or with one black circle any other circle carries any mark, the question will be treated as cancelled.
- (x) The candidates should not remove any paper from the Test-Booklet/Question Paper. Attempting to remove any paper shall be liable to be punished for use of unfair means.
- (xi) Rough work may be done on the blank space provided in the Test-Booklet/Question Paper only.
- (xii) *Mobile phones (even in Switch-off mode) and such other communication/programmable devices are not allowed inside the examination hall.*
- (xiii) No candidate shall be permitted to leave the examination hall before the expiry of the time.

DO NOT OPEN THIS QUESTION BOOKLET UNTIL ASKED TO DO SO.

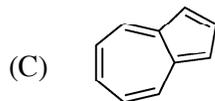
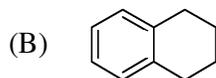
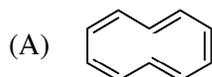
1. Which one of the following structures represent (S)-2-bromo-3,3-dimethylhexane?



2. Which one of the following conformations is the least stable conformation of cyclohexane?

- (A) boat
 (B) half chair
 (C) twist boat
 (D) chair.

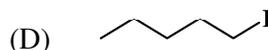
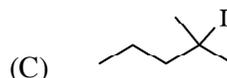
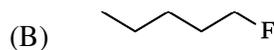
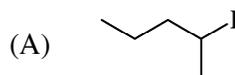
3. Which one of the following compounds is not aromatic?



4. In cyclobutadiene, the highest occupied molecular orbital (HOMO) is

- (A) anti-bonding π -orbital
 (B) non-bonding orbital
 (C) anti-bonding σ -orbital
 (D) bonding π -orbital.

5. Which of the following compounds will react fastest in a substitution reaction with sodium ethoxide in DMF?



6. Which of the following statements is true for elimination reactions?

- (A) E2 reactions are stereoselective but not regioselective
 (B) E1 reactions are regioselective
 (C) E2 reactions are neither stereoselective nor regioselective
 (D) E1 reactions are stereoselective

7. Which of the following reaction conditions will lead to formation of 2,3-dimethylbutan-2-ol as a major product from 2,3-dimethylbut-1-ene?
- (A) $\text{H}_2\text{O}/\text{Br}_2$
 (B) $\text{BH}_3/\text{THF}, \text{H}_2\text{O}_2/\text{NaOH}$
 (C) $\text{H}_2\text{O}/\text{NaOH}$
 (D) $\text{Hg}(\text{OCOCH}_3)_2, \text{NaBH}_4/\text{NaOH}$.
8. Which of the following statement is incorrect for catalytic hydrogenation?
- (A) (Z)-3-methylhex-2-ene gives mixture of diastereomers
 (B) it is a stereoselective reaction
 (C) (E)-3-methylhex-2-ene gives a racemic mixture
 (D) the product is formed by *syn*-addition.
9. If the moment of inertia of a diatomic molecule (XY) is twice that of another diatomic molecule (YZ), then the rotational constant of XY is that of YZ.
- (A) half
 (B) one-fourth
 (C) equal to
 (D) twice.
10. Hyperchromism in electronic absorption spectroscopy corresponds to
- (A) shift to longer λ
 (B) decrease in intensity
 (C) shift to shorter λ
 (D) increase in intensity.
11. Which of the following statement is *incorrect* about CO_2 ?
- (A) It has two degenerate bending modes of vibration
 (B) It has four normal modes of vibration
 (C) It shows four fundamental absorptions peaks in IR
 (D) It has two stretching modes of vibration.
12. The total number of isomers (including constitutional and stereo) for $[\text{Cr}(\text{Br})(\text{SCN})(\text{en})_2]\text{Cl}$ are (where en = ethylenediamine)
- (A) 12
 (B) 15
 (C) 16
 (D) 24.
13. Which of the following statement is false regarding the quantum mechanical description of translational motion in one dimension?
- (A) A particle in 1D-box possesses a zero-point energy
 (B) The particle can be described by wave-function $\psi(x) = A e^{ikx} + B e^{-ikx}$
 (C) Translational energy is quantized for free particle
 (D) The energy of a particle in 1D-box is proportional to n^2 .

14. An electron is travelling in a circle of radius 1 \AA . The energy eigenvalues (in Joule) of the first three rotational wavefunctions are
- (A) $0, 6.10 \times 10^{-19}$ and 2.44×10^{-18}
 (B) $6.10 \times 10^{-19}, 6.10 \times 10^{-19}$ and 2.44×10^{-18}
 (C) $6.10 \times 10^{-19}, 2.44 \times 10^{-18}$ and 5.49×10^{-18}
 (D) $0, 6.10 \times 10^{-19}$ and 6.10×10^{-19} .
15. Which transitions [indicated by the (n, l, m) quantum numbers] of the hydrogen atom occur with the same value of ΔE ?
- (I) $(2, 1, 1) \rightarrow (5, 2, 1)$
 (II) $(2, 1, 1) \rightarrow (4, 2, 1)$
 (III) $(3, 1, 0) \rightarrow (5, 2, 1)$
 (IV) $(3, 2, 0) \rightarrow (5, 1, 0)$.
- (A) (III) and (IV)
 (B) (I) and (II)
 (C) (I), (II) and (IV)
 (D) (II), (III) and (IV).
16. The possible values of quantum number, j for a single electron in d-orbital are
- (A) $1/2$ and $3/2$
 (B) $5/2$ and $3/2$
 (C) 2 and 1
 (D) $+1/2$ and $-1/2$.
17. Arrange the species O_2^+, O_2, O_2^- and O_2^{2-} in increasing order of their bond length.
- (A) $O_2^{2-} < O_2^- < O_2 < O_2^+$
 (B) $O_2^+ < O_2^- < O_2^{2-} < O_2$
 (C) $O_2^+ < O_2 < O_2^- < O_2^{2-}$
 (D) $O_2^+ < O_2^{2-} < O_2 < O_2^-$
18. The molar heat capacity at constant pressure of a certain solid at 10 K is $0.43 \text{ JK}^{-1} \text{ mol}^{-1}$. The molar entropy (in $\text{JK}^{-1} \text{ mol}^{-1}$) of this solid at the same temperature is
- (A) 0.85
 (B) 0.43
 (C) 1.29
 (D) 0.14
19. The equilibrium constant for gas-phase reaction
- $$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
- is 4.00 at 120°C . If the reaction starts with 1 bar of both ethyl acetate and water in a 10 L container, the values of $\Delta_{\text{rxn}} G$ and $\Delta_{\text{rxn}} G^\circ$ at equilibrium are
- (A) -4530 J/mol and 0
 (B) Both 0
 (C) 0 and -4530 J/mol
 (D) Both -4530 J/mol .

20. Which one of the following is correct match of the lattice energy values -3932 ; -3811 and -3791 kJ mol^{-1} with oxides MnO; VO and TiO (Given that the oxides have octahedral geometries and atomic number of Ti: 22; V: 23; Mn: 25).
- (A) MnO: -3791 ; VO: -3932 ; TiO: -3811
 (B) MnO: -3932 ; VO: -3811 ; TiO: -3791
 (C) MnO: -3791 ; VO: -3811 ; TiO: -3932
 (D) MnO: -3811 ; VO: -3791 ; TiO: -3932 .
21. $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ is stabilized by $-1.2\Delta_o$; where $\Delta_o = 151$ kJ/mol ; The absorption maxima of the complex ion will be observed at
- (A) 6.607×10^5 cm^{-1}
 (B) 1.512×10^4 cm^{-1}
 (C) 7.596×10^{27} cm^{-1}
 (D) 1.26×10^4 cm^{-1}
22. Arrange the complexes $[\text{Ni}(\text{CN})_4]^{2-}$; $[\text{MnBr}_4]^{2-}$ and $[\text{Co}(\text{NH}_3)_6]^{2+}$ in increasing order of spin-only magnetic moment.
- (A) $[\text{MnBr}_4]^{2-} < [\text{Ni}(\text{CN})_4]^{2-} < [\text{Co}(\text{NH}_3)_6]^{2+}$
 (B) $[\text{Ni}(\text{CN})_4]^{2-} < [\text{MnBr}_4]^{2-} < [\text{Co}(\text{NH}_3)_6]^{2+}$
 (C) $[\text{Ni}(\text{CN})_4]^{2-} < [\text{Co}(\text{NH}_3)_6]^{2+} < [\text{MnBr}_4]^{2-}$
 (D) $[\text{Co}(\text{NH}_3)_6]^{2+} < [\text{MnBr}_4]^{2-} < [\text{Ni}(\text{CN})_4]^{2-}$
23. A gas phase reaction $\text{A} \rightarrow \text{P}$ follows the mechanism :
- Step 1 : $\text{A} + \text{A} \rightarrow \text{A}^* + \text{A} \quad k_a$
 Step 2 : $\text{A} + \text{A}^* \rightarrow \text{A} + \text{A} \quad k'_a$
 Step 3 : $\text{A}^* \rightarrow \text{P} \quad k_b$
- (Where A^* is energetically excited A due to collision).
- The rate law (steady-state approximation) is given by $\frac{d[\text{P}]}{dt} = \frac{k_a k_b [\text{A}]^2}{(k_b + k'_a [\text{A}])}$. Which of the following statement is incorrect?
- (A) At high pressure, the reaction $\text{A} \rightarrow \text{P}$ can be approximated as unimolecular reaction
 (B) At low pressure, step 1 is the rate determining step
 (C) The reaction follows first order kinetics at low pressure
 (D) The reaction can be approximated as unimolecular if the rate of deactivation by collisions is much greater than the rate of unimolecular decay.
24. A ^1H - ^1H coupling constant for a doublet in a compound X is measured as 5.0 Hz on a 500 MHz NMR spectrometer. Which of the following statement is *incorrect* regarding ^1H NMR of X?
- (A) The difference $\Delta\delta$ for the two peaks of this doublet is 0.05 ppm when measured on a 100 MHz spectrometer.
 (B) The difference $\Delta\delta$ for the two peaks of this doublet depends on the field strength of the spectrometer.

- (C) For this doublet, the coupling constant measured in Hz depends on the field strength of the spectrometer.
- (D) For this doublet, the coupling constant is 5.0 Hz when the spectrum of X is recorded on a 250 MHz NMR spectrometer.
- 25.** Which of the following statements is true about electronic spectroscopy?
- (A) Emission usually occurs at a broad range of energies that are greater than the energies of excitation
- (B) Emission usually occurs at longer wavelength than that of excitation
- (C) Emission always occurs at the exact wavelength of excitation
- (D) Fluorescence emission is a spin forbidden transition.
- 26** The correct statement(s) among the following for intersystem crossing is :
- (A) a radiative process from singlet state to triplet state.
- (B) a non-radiative process from singlet state to triplet state.
- (C) a radiative process from triplet state to singlet state.
- (D) a non-radiative process from triplet state to singlet state.
- 27.** The correct order of octahedral ionic radii of metal ions V^{2+} , Cr^{2+} , and Mn^{2+} in weak ligand field complexes is (At. No., V = 23, Cr = 24, Mn = 25):
- (A) $Mn^{2+} > Cr^{2+} > V^{2+}$
- (B) $Mn^{2+} < Cr^{2+} < V^{2+}$
- (C) $V^{2+} > Mn^{2+} > Cr^{2+}$
- (D) $Cr^{2+} > Mn^{2+} > V^{2+}$
- 28.** Which of the following octahedral complexes will have distorted structure? (At. No., Cu = 29, Ni = 28, Co = 27)
- (i) $[Cu(H_2O)_6]^{2+}$
- (ii) $[Ni(H_2O)_6]^{2+}$
- (iii) $[Ni(NH_3)_2(H_2O)_4]^{2+}$
- (iv) $[Co(H_2O)_6]^{2+}$
- (A) only (i), (ii) and (iii)
- (B) only (i), (ii) and (iv)
- (C) only (i), (iii) and (iv)
- (D) only (i) and (iv)
- 29.** Which one of the following molecules is rotationally Raman inactive?
- (A) H_2
- (B) H_2O
- (C) HCl
- (D) CH_4

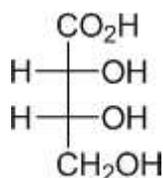
30. The magnetic field strength required for proton magnetic resonance at 60 MHz (Given : $g_N = 5.585$ and $\mu_N = 5.047 \times 10^{-27} \text{ JT}^{-1}$) is :

- (A) 8.46 T
- (B) 2.82 T
- (C) 1.41 T
- (D) 4.23 T.

31. A mixture contains 3g of (+)-2-bromobutane and 2g of (-)-2-bromobutane. The mixture is subsequently placed in a polarimeter and its optical rotation measured. What will be the optical rotation of the mixture, given that (+)-2-bromobutane has a specific rotation of $+23.1^\circ$?

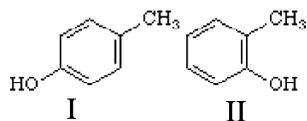
- (A) 11.55°
- (B) 4.62°
- (C) 2.31°
- (D) 9.24° .

32. Which of the following statements is correct about the absolute configuration and optical activity respectively, of the compound shown below :



- (A) (2R, 3R) and optically active
- (B) (2R, 3S) and optically active
- (C) (2S, 3R) and optically inactive
- (D) (2S, 3S) and optically inactive.

33. The chemical structures of two compounds (I and II) are given below. The number of peaks in the ^{13}C -NMR spectrum of these compounds is :

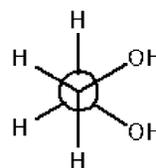


- (A) 7 and 5 for I and II, respectively
- (B) 7 and 7 for I and II, respectively
- (C) 5 and 5 for I and II, respectively
- (D) 5 and 7 for I and II, respectively.

34. The correct increasing order of energies of d orbitals for the complex $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ is (At. No., V = 23)

- (A) $d_{z^2} < d_{x^2-y^2} < d_{xz} = d_{yz} < d_{xy}$
- (B) $d_{x^2-y^2} < d_{z^2} < d_{xy} < d_{xz} = d_{yz}$
- (C) $d_{xy} < d_{xz} = d_{yz} < d_{x^2-y^2} < d_{z^2}$
- (D) $d_{xz} = d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$

35. The most stable conformation for 1,2-ethanediol (ethylene glycol) is shown below. It is the most stable conformation because :



- (A) this corresponds to an anti conformation.

- (B) it is stabilized by intramolecular hydrogen bonding.
- (C) usually gauche conformations possess overall minimum energy.
- (D) it has the highest energy of all the possibilities.
- 36.** Most stable conformation of *meso*-3,4-dimethylhexane along C3-C4 bond contains
- (A) a center of symmetry
- (B) both plane of symmetry and center of symmetry
- (C) a plane of symmetry
- (D) neither plane of symmetry nor center of symmetry.
- 37.** The state of the electron with mass "m" is described by the wavefunction $\psi = (2)^{1/2} \sin k\pi x$, where k is some constant. Assume that the potential energy is zero, what is the energy of the electron?
- (A) $k^2 h^2 \pi^2 / 2m$
- (B) $k^2 \hbar^2 / 2m$
- (C) $k^2 h^2 / 2 \pi^2 m$
- (D) $k^2 \hbar^2 \pi^2 / 2m$.
- 38.** The wavefunction for the motion of a particle of mass, M, on a 2D ring of radius "r" is given as $\psi(\phi) = (2\pi)^{-1/2} e^{im\phi}$, where $m = 0, \pm 1, \pm 2 \dots$. Which of the following statement(s) is/are correct?
- (I) Probability density associated with it will be $1/2\pi$
- (II) Angular momentum of the particle is precisely defined. So uncertainty principle is violated.
- (III) No zero point energy is associated with the particle
- (IV) All the energy levels are two-fold degenerate
- (A) Both (I) and (II) are correct
- (B) Both (I) and (III) are correct
- (C) Both (II) and (III) are correct
- (D) Both (II) and (IV) are correct.
- 39.** ----- C_2 and N_2 molecules are, respectively.
- (A) paramagnetic and paramagnetic
- (B) paramagnetic and diamagnetic
- (C) diamagnetic and diamagnetic
- (D) diamagnetic and paramagnetic.
- 40.** Electrocyclization (ring closing) of (2Z, 4Z, 6E)-octa-2,4,6-triene under thermal and photochemical conditions will give
- (A) only *cis*-5,6-dimethylcyclohexa-1,3-diene
- (B) only *trans*-5,6-dimethylcyclohexa-1,3-diene
- (C) *cis*-5,6-dimethylcyclohexa-1,3-diene and *trans*-5,6-dimethylcyclohexa-1,3-diene, respectively
- (D) *trans*-5,6-dimethylcyclohexa-1,3-diene and *cis*-5,6-dimethylcyclohexa-1,3-diene, respectively

41. Racemization of a chiral complex $[\text{Cr}(\text{ox})_3]^{3-}$ is least likely to occur by
- a dissociate pathway
 - a pathway involving a 5-coordinate species in which one ox^{2-} ligand is monodenate
 - the Ray–Dutt twist mechanism
 - the Bailar twist mechanism.
42. Which of the following has a center of inversion?
- CO_2
 - C_2H_2
 - BF_3
 - SO_4^{2-} .
- (i) and (ii) only
 - (i) and (iii) only
 - (i) and (iv) only
 - (ii) and (iii) only.
43. The p^5 electronic configuration is equivalent to the term
- 3P
 - 2P
 - 3F
 - 4P .
44. A student recorded a polarogram of 2.0 mM Cd^{2+} solution but forgot to add KCl solution. What type of error can you expect in these results.
- Only migration current will be observed
 - Only diffusion current will be observed
 - Both migration current as diffusion current will be observed
 - Both catalytic current, as well as diffusion current will be observed.
45. The low temperature (-98°C) ^{19}F NMR spectrum of SF_4 shows doubles of triples. It is consistent with the point group symmetry.
- C_{3v}
 - C_{4v}
 - T_d
 - C_{2v} .
46. The total numbers of fine and hyperfine EPR lines expected for an octahedral high spin $\text{Mn}(\text{II})$ complexes are respectively ($I = 5/2$ for Mn)
- 3 and 30
 - 5 and 33
 - 5 and 30
 - 4 and 24.

47. The Kiliani-Fischer reaction of an aldopentose
- (A) is a diastereoselective reaction
 - (B) is an enantioselective reaction
 - (C) gives a mixture of aldohexoses differing in configuration at C₆
 - (D) gives a racemic mixture.
48. An octapeptide has the composition Ala₂, Gly₂, Phe₂, Ser₂. The N-terminal unit is Ala. Cleavage of the octapeptide by chymotrysin gives a single tetrapeptide, having Ala as its N-terminal group. Among the products of random hydrolysis is a Phe-Ala-Gly tripeptide fragment. What is the primary structure of the octapeptide?
- (A) Ala-Gly-Ser-Phe-Phe-Ser-Gly-Ala
 - (B) Ala-Ser-Gly-Phe-Ala-Gly-Ser-Phe
 - (C) Ala-Ser-Gly-Phe-Ala-Ser-Gly-Phe
 - (D) Ala-Gly-Ser-Phe-Ala-Gly-Ser-Phe.
49. The slope of the curve between log T vs log V in a reversible adiabatic expansion of a gas is
- (A) $1 - \gamma$
 - (B) $\gamma - 1$
 - (C) γ
 - (D) $(1 - \gamma)^{-1}$
- (where $\gamma = c_p / c_v$).
50. When d^2/x^2 operates on the function $6 \sin(4x)$, we find
- (A) The function is an eigenfunction with eigenvalue-96
 - (B) The function is an eigenfunction with eigenvalue-16
 - (C) The function is an eigenfunction with eigenvalue-16
 - (D) The function is an eigenfunction.

ROUGH WORK