I. Choose one correct answer for each of the following questions. (36%, 2% each)

1. How many chiral carbons are there in an open-chain aldohexose such as glucose?
   (A) 2 (B) 3 (C) 4 (D) 5

2. Give the products from the reaction of HIO₄ with a ketohexose
   HOCH₂CHOHCHOHCHOHCOCH₂OH
   (A) 5HCOOH + H₂C=O  (B) 4HCOOH + H₂C=O
   (C) 3HCOOH + 3 H₂C=O (D) 3HCOOH + 2H₂C=O + CO₂

3. What is the smallest aldose able to form a cyclic hemiacetal?
   (A) triose  (B) tetrose  (C) pentose  (D) hexose

4. The specific rotation for α- and β-anomers of glucose is +112° and +19°, respectively. For a constant equilibrium mixture with a specific rotation of +52.7°, calculate the % composition of each anomer.
   (A) α: 45%, β: 55%  (B) α: 63.8%, β: 36.2%
   (C) α: 36.2%, β: 63.8% (D) α: 55%, β: 45%

5. Which of the following amino acids have heterocyclic structures?
   I. Lysine  II. Histidine  III. Proline  IV. Tryptophane
   (A) II, IV  (B) II, III, IV  (C) I, II, IV  (D) I, II, III

6. What is the pI value of Histidine with pKₐ₁, pKₐ₂, pKₐ₃ corresponding to 1.82, 6.0, and 9.7, respectively?
   (A) 7.59  (B) 3.91  (C) 5.33  (D) 7.82

7. Which of the following statements regarding addition and removal of blocking group during peptide synthesis is correct?
   (A) The side chain of Ser can be blocked by acetyl group and deprotected by H₂/Pd
   (B) The side chain of Lys can be blocked by p-toluenesulfonyl group and deprotected by CF₃COOH
   (C) The side chain of Glu can be blocked by benzyl ester and deprotected by weak alkali
   (D) The side chain of His can be blocked by N-benzyl group and deprotected by sodium in liquid ammonia
8. The artificial sweetener is a synthetic dipeptide AspPhe. How many stereoisomers are possible?
   (A) 2 (B) 4 (C) 6 (D) 8

9. Place the following compounds in increasing order of basicity:
   I. PhNH₂  II. Piperidine  III. Pyridine  IV. Pyrrol
   (A) I, II, III, IV  (B) II, IV, III, I  (C) III, II, IV, I  (D) IV, I, III, II

10. Which of the following statements is correct?
   (A) The dipole moments of phenol and methanol are in opposite directions
   (B) o-Nitrophenol has higher boiling point than the m-isomer
   (C) o-Hydroxybenzaldehyde has higher boiling point than the p-isomer
   (D) Phenol has lower boiling point than benzenethiol

11. Place the following compounds in decreasing order of acidity:
   I. phenol  II. o-nitrophenol  III. m-nitrophenol  IV. p-nitrophenol
   (A) I, II, III, IV  (B) II, IV, I, III  (C) III, IV, I  (D) IV, II, III, I

12. Based on the inductive effect, which of the following differences in acidity is correct?
   (A) Me₃SiCH₂COOH > Me₂CCH₂COOH  (B) ClCH₂COOH > NO₂CH₂COOH
   (C) ClCH₂COOH > CIC₂H₂CH₂COOH  (D) Cl₂CHCOOH > Cl₃COO⁻

13. Neutralization of 0.3504 g of an acid requites of 27.24 ml of 0.1500 M NaOH, and the molecular
   weight is found from mass-spectral data to be 172.1 g/mol. How many ionizable H’s are there in the
   acid?
   (A) 1  (B) 2  (C) 3  (D) 4

14. What is the rearrangement of the oxime of propanal in the presence of conc. H₂SO₄ and PCl₅?
   (A) PhNHCOPh  (B) CH₃CONNHCH₃
   (C) CH₃CH₂CONH₂  (D) HCONHCH₂CH₃
15. Which of the following descriptions about solvomercuration-demercuration of an alkene is correct?
   (A) Presence of rearrangement  (B) Anti-Markovnikov addition
   (C) Syn addition of Hg(COCCF_3)_2  (D) Anti addition of R’-OH

16. Which of the following chemical tests can not distinguish between each pair of compounds?
   (A) (CH_3)_2CHOH and (CH_3)_2CHSH; Hg^{2+}
   (B) CH_3CH_2SCH_3 and (CH_3)_2CHSH; NaOH_{aq}
   (C) CH_3CH_2CH_2OH and (CH_3)_2CHOH; I_2/OH^{-}
   (D) (CH_3)_2C(OH)CH_2CH_3 and CH_3CH_2CH(OH)CH_2CH_3; Cr^{3+}

17. Which of the following compounds are aromatic?
   I. cycloheptatrienyl carbocation  II. cyclooctatetraene
   III. 2,4,6-trinitrotoluene  IV. cyclobutadiene
   (A) I, III  (B) II, IV  (C) I, II, III  (D) II, III, IV

18. Which of the following molecules are chiral?
   I. 3-methyl-1-pentene  II. 2,3-pentadiene  III. 2R, 5S-dimethyloctane  IV. Glycine
   (A) I, II  (B) I, III  (C) II, IV  (D) I, IV
II. Provide rational explanations, mechanisms, or calculations for each of the following questions.

(20%, 4% each)

1. A tripeptide W is hydrolyzed completely to 2 eq. of Glu and 1 eq. each of Ala and NH₃. W has only 1 free carboxyl group and does not react with 2,4-dinitrofluorobenzene. Ala is released first when W is treated with carboxypeptidase. Determine the structure of X and briefly explain.

2. Draw a mechanism to explain the isolation of a tetradeuterated product from the reaction of CH₂CH=CHCHO with OD⁺ in D₂O.

3. Balance the following oxidation reaction (in base) by the ion-electron (half cell) method.

\[ \text{PhCH}_2\text{OH} + \text{KMnO}_4 \rightarrow \text{PhCOOH} + \text{MnO}_2 + \text{H}_2\text{O} + \text{OH}^- \]

4. The reduction of 4-tert-butylicyclohexanone with LiAlH₄ gives mainly the trans alcohol (90%), but with Si₃BH₄, the product is mainly cis alcohol (88%). Draw the structures of the alcohols and explain the different product distributions.

5. Optically active (2S,3R)-3-bromo-2-butanol (X) reacts with KOH and MeOH to give an optically active epoxide (Y). Y is treated with KOH in H₂O to give 2,3-butanediol (Z).

(a) Write three-dimensional structures of X, Y, and Z.

(b) Does Z show optical rotation? Explain.
III. Spectroscopy

Choose one correct answer from each of the following questions.

1. Amines P, Q, R, S each have their parent cation peaks at m/z = 59. The highest intensity peaks are at m/z = 44 for P and Q, 30 for R, and 58 for S. Which one of them contains a tertiary amine?
   (A) P  (B) Q  (C) R  (D) S  (E) none of them

2. The IR spectrum of a dilute solution of cis-3-fluorocyclohexanol shows a broader, lower-frequency O-H stretching peak than does the trans isomer. Which of the following is the main determining factor?
   (A) Van der Waals force  (B) dipole-dipole interaction (C) intramolecular hydrogen bond (D) intermolecular hydrogen bond  (E) steric hinderance

3. The $^{13}$C-NMR spectra of cis-decalin ($C_{10}H_{18}$, consists of two fused cyclohexane rings) can exhibit very different characteristics over a wide temperature range due to the conformational exchange of the molecule. At 90 °C the conformational exchange is very fast. What would you expect to see in the spectrum? The spectrum shows
   (A) 4 peaks of relative intensities 2:1:1:1 (B) 5 peaks of relative intensities 1:1:1:1:1 (C) 2 peaks of relative intensities 4:1 (D) one peak (E) 3 peaks of relative intensities 2:2:1

4. Follow the previous question. What would you expect to see in the $^{13}$C-NMR spectrum when the temperature decreases to -50 °C, where the conformational exchange is slow? The spectrum shows
   (A) 4 peaks of relative intensities 2:1:1:1 (B) 5 peaks of relative intensities 1:1:1:1:1 (C) 2 peaks of relative intensities 4:1 (D) one peak (E) 3 peaks of relative intensities 2:2:1

5. Which of the following compounds could give rise to the infrared spectrum shown below? (A) acetanilide (B) aniline (C) $N,N$-dimethylformamide (D) $m$-anisidine (E) $n$-butylamine
6. Which of the following compounds is consistent with the $^1$H-NMR spectrum shown below? (A) $n$-propyl formate (B) methyl propionate (C) ethyl acetate (D) methacrylic acid (E) ethyl acetate

![NMR Spectrum](image1)

7. Which of the following compounds is consistent with the $^1$H-NMR spectrum shown below? (A) 2,3-xylenol (B) benzyl methyl ether (C) $\alpha$-phenylethyl alcohol (D) 3,5-xylenol (E) $\beta$-phenylethyl alcohol

![NMR Spectrum](image2)

8. Which of the following statements is wrong? (A) IR absorption is due to molecular vibration (B) NMR signal is due to the radioactivity of nucleus under the influence of external magnetic field (C) The UV/Visible absorption for organic compounds involves the electronic transition in the $\pi$ orbitals (D) Mass spectrometry resolves particles according to the charge/mass ratio (E) The bending frequency is often smaller than the stretching frequency of a molecular bond.
9. Geraniol, C_{10}H_{18}O, a terpene found in rose oil, gives the infrared, $^{13}$C-NMR and $^1$H-NMR spectra shown below. Based on the spectra, which of following statements is wrong? (A) Geraniol is an aliphatic compound (B) Geraniol is a primary alcohol (C) Geraniol contains only one carbon-carbon double bond (D) Geraniol has three methyl groups (E) There is only one labile proton in Geraniol.

![Infrared Spectrum of Geraniol](image1)

![NMR Spectra of Geraniol](image2)
10. Deduce from the spectra below, the compound TT is (A) Benzyl acetate (B) hydrocinnamic acid \( \text{C}_8\text{H}_7\text{CH}_2\text{CH}_2\text{COOH} \) (C) cyclohexyl acetate (D) methyl phenylacetate (E) none of the above.
IV. Predict major product for each of the following reactions. (24%, 2% each)

1. 

2. 

3. 

4. 

5. 

6. 

\[
\text{O} = \text{C} - \text{NH}_2 + \text{O} = \text{C} - \text{CH} - \text{C} - \text{C} - \text{OEt} \quad \text{OEt}^- \rightarrow F
\]
7. 
Claisen rearrangement

8. 
\[ p\text{-quinone} + \quad \rightarrow \quad H \]

9. 
\[ \overset{\text{C}_{6}H_{5}COOH}{\text{Ph} - C - \overset{\text{C}_{6}H_{5}COOH}{\text{Ph}}} \rightarrow I \]

10. 
\[ \text{Acetophenone} \rightarrow J \]

11. 
\[ \text{PhCH}_{2}\text{CH}_{2}\text{CH}_{2}OH \rightarrow K \]

12. 
\[ o\text{-FC}_{6}H_{4}\text{OMe} \rightarrow L \]