Subject: GENERAL CHEMISTRY CHEM F111	Comprehensive Examination (Open Book)
Max. Marks: 85	Duration: 120 minutes	Date: December 07, 2017 (AN)

NOTE: There are SIX questions in all. Attempt all the questions. Start answering each question on a fresh page and answer all parts of the question together. Pencil should not be used. Symbols have usual meanings. Do not scribble on the question paper.
USEFUL DATA: $c = 3 \times 10^8$ m/s; $m_e = 9.109 \times 10^{-31}$ kg; 1 amu $= 1.66 \times 10^{-27}$ kg; $a_0 = 0.529$ Å; $h = 6.626 \times 10^{-34}$ Js; $k = 1.38 \times 10^{-23}$ J.K^{-1}; $R_H = 109680$ cm^{-1};

Q1. (a) Photoelectrons ejected from a metal surface were subjected to scattering experiments where the smallest wavelength recorded for the electrons was 1.319 nm. If workfunction of the metal is 2.52 eV, find the frequency (in THz) of the electromagnetic radiation incident on the metal surface. If the radiation incident on the surface of the metal happens to be the most intense radiation emited from surface of a hot filament (and filtered before being incident on the metal surface), estimate the temperature of the filament. Assume the relativistic effects in all the processes to be negligible. **[7]**

(b) Particle is confined to move in a 2D box with potential energy defined as V(x,y)=0 for 0≤x≤L; 0≤y≤2L and infinite otherwise. Obtain the energies E_{n_x,n_y} of first four energy levels and arrange them in the ascending order. Write the wavefunction for the lowest excited non-degenerate energy level. **[4+1]**

(c) Recall that calculation of components of linear momentum of a system requires evaluation of the corresponding first order (partial) derivatives of the wavefunction of the system. Consider the 1s-wavefunction of hydrogen atom: $\Psi_{1s} = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$. $(r = \sqrt{x^2 + y^2 + z^2})$ At nucleus, is the wavefunction differentiable *w.r.t.* x? In no more than two sentences, comment on the well-behavedness of the wavefunction. **[2]**

Q2. (a) Assume you are working in a molecular spectroscopy laboratory which is equipped with instruments to perform four major spectroscopic measurements, namely, (i) Rotational spectroscopy, (ii) Rotational Raman spectroscopy, (iii) Vibrational spectroscopy, and (iv) Vibrational Raman spectroscopy. You have been assigned to determine the molecular structure of hydrogen peroxide (H_2O_2). H_2O_2 exists in the form of three different Conformers depending on the dihedral angle ($d_\theta = \angle$H-O-O-H). Dihedral angles of those three conformers are $d_\theta = 0°$ (Conformer-I), $d_\theta = 80°$ (Conformer-II), and $d_\theta = 180°$ (Conformer-III). You may use any one of the above mentioned spectroscopic techniques to determine the structure of the three conformers. Choice is yours but that should be logical and less complicated. In general, scattering experiment is challenging and complicated compared to techniques based on absorption/transmission mode. You have also recorded vibrational and vibrational Raman spectra of H_2O_2 as described in the following table;

Mode description	Vibration (cm^{-1}), H_2O_2	Raman (cm^{-1}), H_2O_2	Mode description	Vibration (cm^{-1}), H_2O_2	Raman (cm^{-1}), H_2O_2
ν_1	3607	3606	ν_4	317	-
ν_2	-	1393	ν_5	3608	-
ν_3	-	863	ν_6	1266	-

Answer the following questions after you read the above description carefully:
1) Identify spectroscopic technique to determine the structure of a) Conformer-I, b) Conformer-II, and c) Conformer-III. Justify your choice with key words which should not be more than one line. **[4]**
2) Identify possible conformers of H_2O_2 which/those are responsible for the observed vibrational and vibrational Raman spectra. Justify your answer in brief. **[3]**
3) ν_1 and ν_3 modes represent stretching vibration for H_2O_2 molecule. The corresponding transitions in D_2O_2 are 2669 cm^{-1} (ν_1) and 867 cm^{-1} (ν_3). Identify with justification ν_1 and ν_3 modes of H_2O_2. **[3]**

(b) In proton NMR spectra of CH_3CH_2X, the chemical shift of the CH_3 protons is $\delta = 1.26$ and that of the CH_2 protons is $\delta = 3.36$. What is the difference in local magnetic field between two regions of the molecule when the NMR experiment has been conducted with 16.5 Tesla magnetic field? **[2]**

Figure 2c

(c) ^1H-NMR spectra of the same compound (CH_3CH_2X) is recorded in 600 MHz spectrometer and is depicted in Figure 2c. The measured J value for CH_3CH_2X in 300 MHz spectrometer is $J = 7.21$ Hz. Determine values of A, and B in frequency domain. **[2]**
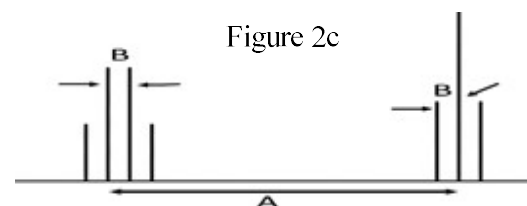
Q3. Consider the following scheme and answer appropriately.
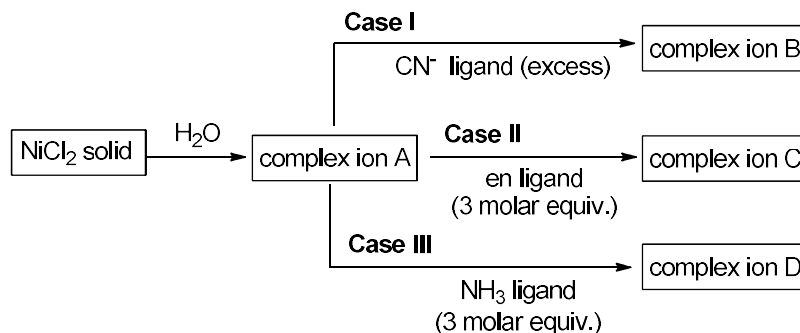
(a) Identify the complex ions A, B, C, D mentioning their respective geometries. Write in proper format as $[M(L_1)_m(L_2)_n]^{p(+/-)}$, where M may represents the metal center, L_1, L_2 are ligands with m & n as their respective numbers and p(+/-) is the charge of the complex ion (positive or negative), as appropriate. **[6]**

**(b)** State whether complex ion A and complex ion B show paramagnetic or diamagnetic behavior with ONE LINE explanations only **[4]**

(c) Write (No diagrams required) the d-orbital levels in an increasing order of energy for complex ion B and calculate the CFSE if $\Delta_o = 22,000$ cm^{-1} and P = 16020 cm^{-1} approximately. **[2]**

(d) Is the complex ion C chiral or achiral? **[1]**

(e) Write all the possible geometrical isomers of the complex ion D. **[2]**

Q4. Consider the following high-spin Cr(II) octahedral complex, answer the given questions.
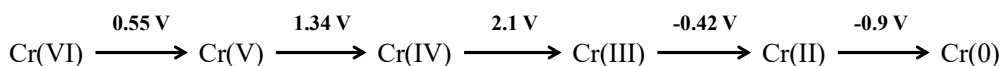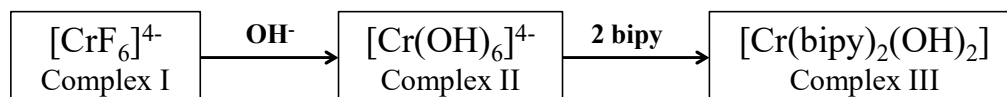

(Latimer diagram of Cr species)

(a) How many band(s) is/are expected theoretically in electronic spectrum based on the ground state term in complex I? (No diagram required) Assign the electronic transition arising from ground state term. **[1+2]**

(b) Which of the geometry (tetragonal elongation or compression) is expected to observe for complex II? Justify your answer in no more than 2-3 lines. **[1+2]**

(c) What is/are the driving force (s) behind the conversion of complex II to complex III? Calculate the overall formation constant (β) in "log$_{10}$" form for complex III at 40 °C, if the standard enthalpy and entropy changes are -8.1 kJ/mol and 0.152 kJ/mol, respectively. [R = 8.313 J/(mol.K)] **[1+3]**

(d) Based on the reduction potential value from Latimer diagram of Cr species, conversion of Cr(V) to Cr(VI) is not spontaneous, however, Cr(V) converts to Cr(VI). Justify your answer. **[3]**

Q5. (a) A particular stereoisomer of *Muscarine* (Figure **5ai**) possessing an absolute configuration, (2*S*,4*R*,5*S*) is present in the mushroom *Amanita muscaria*. Identify the atoms/groups that will substitute A, B, C, D in the given form (Figure **5aii**) to illustrate its correct stereochemistry at carbon labeled as 4 & 5. **[4]**

Muscarine (Racemic)
Figure **5ai**

(2S,4R,5S)-Muscarine
Figure **5aii**
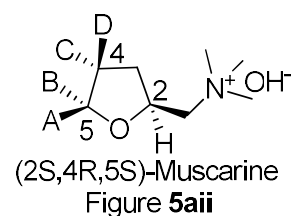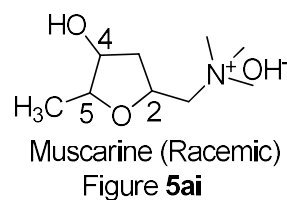
(b) (i) Identify X, Y, Z in the given Newman projection form (Figure **5b**) to obtain the most stable conformer of (3*R*,4*S*)-3,4-dimethylhexane and calculate its energy. (*Given: the gauche interaction values for ethyl-ethyl, ethyl-methyl and methyl-methyl are 4.6, 4.2 and 3.8 kJ/mol, respectively and Assuming ethyl-H, methyl-H gauche interaction values to be zero*). (ii) Comment on the optical activity of the compound. **[4+1]**
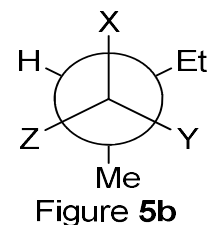

Figure **5b**

(c) (i) Referring the chair conformation (Figure **5c**), identify the atoms/alkyl groups which upon replacing M, N, O, P will yield the lowest energy chair conformation of *trans*-1-(*t*-butyl)-3-methylcyclohexane. (ii) Convert the resultant lowest energy chair conformer into its planar projection form indicating dash-wedge notation of the substituents. **[2+1]**
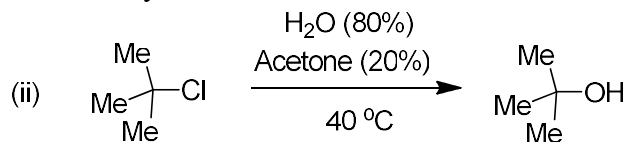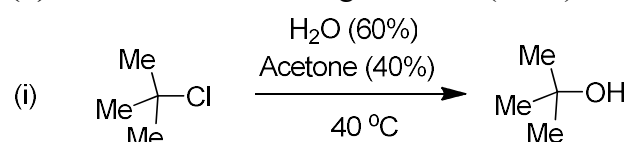

Figure **5c**
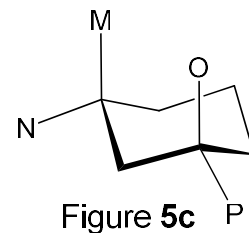
(d) How many CH_3-H gauche interactions are present in the lowest energy chair conformation of *cis*-1-(*t*-butyl)-3-methylcyclohexane? **[2]**

Q6. (a) Write the structure of product(s) for the following reactions with appropriate stereochemistry, wherever applicable. **[2×5 = 10]**

(i)

m-CPBA
Heat

(ii)

Br_2/H_2O

(iii)

+ heat

(iv)

Heat

(v)

i) CH_3I, heat
ii) Ag_2O/H_2O
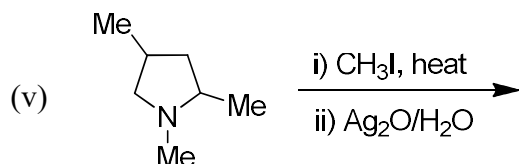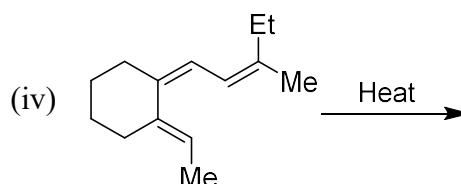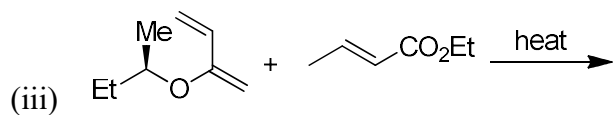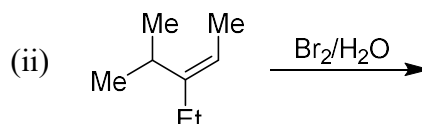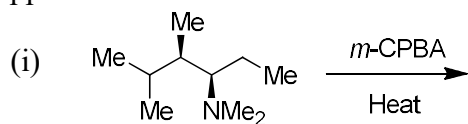
(b) Which of the following reactions (i & ii) will be faster and why? **[2]**

(i)

H_2O (60%)
Acetone (40%)
40 °C

(ii)

H_2O (80%)
Acetone (20%)
40 °C

(c) Indicate reaction conditions/reagents, propose appropriate synthesis of 1-bromo-3-propylbenzene from benzene. **[3]**

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CHEM F111 GENERAL CHEMISTRY	**Comprehensive Examination Part-I (Closed Book)**
Max. Marks: 50 **Duration: 60 minutes**	**Date: December 07, 2017**

NOTE: *There are twenty five questions in all. Check the answer sheet **CODE (X or Y)** with that of the question paper. Indicate the most appropriate answer by entering **A, B, C, or D** in **CAPITAL LETTER ONLY** in boxes provided in separate answer sheet. Do not **overwrite**. Do not use pencil. Each question carries **02 marks** and **0.5 marks** will be deduced for every incorrect answer.*
USEFUL DATA: Atomic number: F = 9; Cr = 24; Co = 27; Fe = 26; Cu = 29.

Q1. The wavefunction for 1s orbital of a hydrogenic atom is given by $\Psi_{n,l,m} = \left(\frac{Z^3}{\pi a^3}\right)^{1/2} e^{\frac{-Zr}{a}}$, where Z = Nuclear charge and $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$, other symbols have usual meaning. The radial distribution function for the orbital is given by

(A) $4\pi r^2 \left(\frac{Z^3}{\pi a^3}\right)^{1/2} e^{\frac{-Zr}{a}}$ (B) $4\pi r^2 \left(\frac{Z^3}{\pi a^3}\right) e^{\frac{-2Zr}{a}}$ (C) $\left(\frac{Z^3}{\pi a^3}\right)^{1/2} e^{\frac{-Zr}{a}}$ (D) $r^2 \left(\frac{Z^3}{\pi a^3}\right) e^{\frac{-Z^2 r^2}{a^2}}$

Q2. The energy eigen value for hydrogenic atom is given by $E = -\frac{Z^2 e^4 \mu}{8\varepsilon_0^2 h^2 n^2}$. Using orbital approximation and neglecting electron-electron repulsion, the expression of the electronic energy of helium atom will be

(A) $E = -\frac{e^4 \mu}{2\varepsilon_0^2 h^2 n^2}$ (B) $E = -\frac{e^4 \mu}{4\varepsilon_0^2 h^2 n^2}$ (C) $E = -\frac{e^4 \mu}{\varepsilon_0^2 h^2 n^2}$ (D) $E = -\frac{e^4 \mu}{8\varepsilon_0^2 h^2 n^2}$

Q3. ^{33}S has a nuclear spin of 3/2. The number of nuclear spin states and their energy in a magnetic field B will be (where g = nuclear g-factor and μ = nuclear magneton)

(A) *Two spin states, Energy of spin states*: $-\frac{1}{2}g\mu B$, $+\frac{1}{2}g\mu B$

(B) *Two spin states, Energy of spin states*: $-\frac{3}{2}g\mu B$, $+\frac{3}{2}g\mu B$

(C) *Four spin states, Energy of spin states*: $-\frac{3}{2}g\mu B$, $-\frac{1}{2}g\mu B$, $+\frac{1}{2}g\mu B$, $+\frac{3}{2}g\mu B$

(D) *Five spin states; Energy of spin states*: $-\frac{3}{2}g\mu B$, $-\frac{1}{2}g\mu B$, 0, $+\frac{1}{2}g\mu B$, $+\frac{3}{2}g\mu B$

Q4. The emission spectra of sodium atom shows a pair of closely spaced lines separated by 6Å. These are due to the transitions from higher energy electronic states to lowest energy ground state of Na. Which of the following correctly represent these electronic transitions in Na?

(A) $^2P_{1/2} \rightarrow ^2S_{1/2}$ and $^2P_{3/2} \rightarrow ^2S_{1/2}$ (B) $^2P_{1/2} \rightarrow ^2S_{1/2}$ and $^2D_{5/2} \rightarrow ^2S_{1/2}$

(C) $^3P_{1/2} \rightarrow ^2S_{1/2}$ and $^3P_{3/2} \rightarrow ^2S_{1/2}$ (D) $^3P_{1/2} \rightarrow ^3S_{1/2}$ and $^3P_{3/2} \rightarrow ^3S_{1/2}$

Q5. ^{1}H-NMR of a hydrocarbon has three peaks. The name of the hydrocarbon must be:
(A) cyclopentane   (B) 2-methylbutane   (C) *n*-pentane   (D) 2,2-dimethylpropane

Q6. Arrange the following species in increasing order of bond length: F_2, F_2^+, and F_2^-
(A) $F_2 > F_2^+ > F_2^-$ (B) $F_2^- > F_2 > F_2^+$ (C) $F_2^- > F_2^+ > F_2$ (D) $F_2^+ > F_2 > F_2^-$

Q7. The notations '*g*' and '*u*' designated for two center π-bonding and antibonding orbitals, is based on
(A) symmetry of the orbitals w.r.t. a hypothetical point at the center of the internuclear axis
(B) existence of a mirror plane along the internuclear axis
(C) existence of an axis of symmetry along the internuclear axis
(D) existence of differently sized opposite lobes

Q8. In a linear metal complex, considering the approach of ligands along the z axis, the d orbitals of the metal
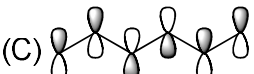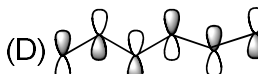(A) remain degenerate   (B) split into set of two   (C) split into set of three   (D) split into set of four

Q9. The complex CoL_2X_2, (where L= triphenyl phosphine and X= Cl⁻) is optically inactive and it has
(A) center of symmetry   (B) two planes of symmetry   (C) three planes of symmetry   (D) one plane of symmetry

Q10. The EAN value of which of the complex is not 36.
(A) $[Cr(CO)_6]$ (B) $[Co(NH_3)_6]^{3+}$ (C) $[Cu(CN)_4]^{3-}$ (D) $[Fe(CN)_6]^{3-}$

Q11. Which one of the following represents the LUMO of 1,3,5-hexatriene?

(A)   (B)   (C)   (D)

Q12. Which one of the following statements is true?
(A) Ethoxide ion is more nucleophilic and more basic than *t*-butoxide
(B) Ethoxide ion is more nucleophilic and less basic than *t*-butoxide
(C) Ethoxide ion is less nucleophilic and more basic than *t*-butoxide
(D) Ethoxide ion is less nucleophilic and less basic than *t*-butoxide

Q13. Which one of the following statements regarding Friedel-Crafts reaction is true?
(A) Friedel-Crafts acylation of nitrobenzene readily gives 3-nitroacetophenone
(B) Friedel-Crafts alkylation of benzene with *n*-butylbromide yields 1-butylbenzene exclusively
(C) Friedel-Crafts acylation of aniline readily gives *o*-aminoacetophenone and *p*-aminoacetophenone
(D) Aryl and vinyl halides cannot be used in Friedel-Crafts alkylation

Q14. Under which of the given condition(s), an electrocyclic reaction is proceeded in a conjugated alkene containing even number of π-bonds: (i) conrotatory, thermal; (ii) conrotatory, photochemical; (iii) disrotatory, thermal; (iv) disrotatory, photochemical.
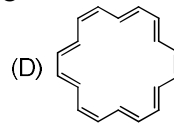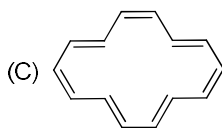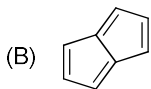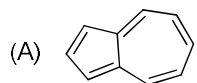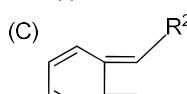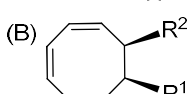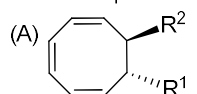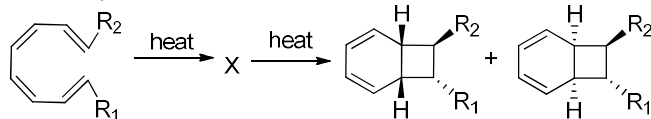(A) only I (B) only ii (C) i or iv (D) ii or iii

Q15. Which one of the following compounds is not aromatic according to Hückel's rule?

(A)   (B)   (C)   (D)

Q16. Which one of the compounds is the likely intermediate (X) for the following chemical transformation involving two electrocyclic reactions?

(A)   (B)   (C)   (D)
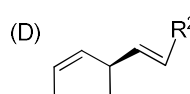
Q17. Which one of the following dimethylcyclohexane exists as a pair of conformational enantiomers?
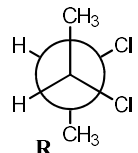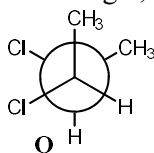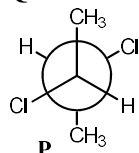(A) *trans*-1,2–Dimethylcyclohexane (B) *trans*-1,3–Dimethylcyclohexane
(C) *cis*-1,2–Dimethylcyclohexane (D) *cis*-1,3–Dimethylcyclohexane

Q18. Among the following 2,3-dichlorobutanes (P,Q,R,S), the configurational diastereomeric pair is ?
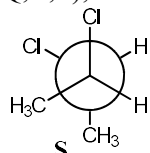
(A) P and S (B) P and R (C) S and Q (D) P and Q

**Q19.** S_N2 reactions involving chiral alkyl halide usually proceed with
(A) slightly more retention than inversion (B) slightly more inversion than retention
(C) inversion of configuration (D) retention of configuration

Q20. An optically inactive compound **Y** (molecular formula C_8H_{14}) undergoes catalytic hydrogenation to give optically inactive product. The structure of **Y** is

(A)   (B)   (C)   (D)
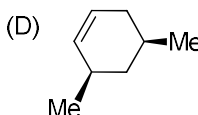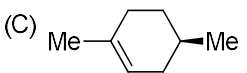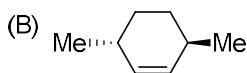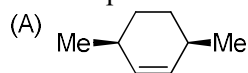
Q21. Which one of following statements is true for hydration of 2-methylbut-1-ene?
(A) Hydration by oxymercuration-demercuration gives anti-Markovnikov orientation.
(B) Hydration by hydroboration-oxidation gives Markovnikov product.
(C) Hydration by oxymercuration-demercuration is a stereospecific reaction.
(D) Acid catalyzed hydration will give racemic product.

Q22. Which among the following will show geometric isomerism?
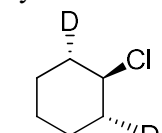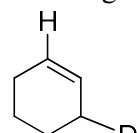(A) 2,3-dimethylpent-2-ene (B) 3,4-dimethylhex-3-ene (C) 2-methyl-2-butene (D) 1-pentene
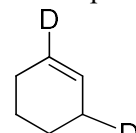
Q23. Base catalyzed E2 elimination of chlorocyclohexanes **1** & **2** give monodeuterated cyclohexene **P** and/or dideuterated cyclohexene **Q**. Which one of the following best indicates the most probable selectivities of two reactions?
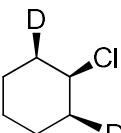

(A) P from both 1 and 2 (B) Q from both 1 and 2 (C) P from 1 and Q from 2 (D) Q from 1 and P from 2

Q24. Which one of the following you would use to resolve a racemic carboxylic acid?
(A) Chiral acid (B) Racemic acid (C) Chiral amine (D) Racemic amine

Q25. The observed rotation for an enantiomeric mixture of compound **Z** is + 95°, while the rotation of its pure enantiomer is + 102°. The ratio of enantiomers present in the mixture is
(A) 93:7 (B) 96.5 : 3.5 (C) 95:5 (D) 95.6 : 4.5

Instructions: *Check the answer sheet **CODE (X or Y)** with that of the question paper. Indicate the most appropriate answer by entering **A, B, C, or D** in **CAPITAL LETTER ONLY** in boxes provided in this answer sheet. Do not **overwrite.** Do not use pencil. Each question carries **02 marks** and **0.5 marks** will be deduced for every incorrect answer.*

Q.1	B		Q.14	C
Q.2	C		Q.15	B
Q.3	C		Q.16	A
Q.4	A		Q.17	C
Q.5	C		Q.18	B
Q.6	B		Q.19	C
Q.7	A		Q.20	A
Q.8	C		Q.21	D
Q.9	B		Q.22	B
Q.10	D		Q.23	C
Q.11	D		Q.24	C
Q.12	B		Q.25	B
Q.13	D			

For Examiner:

Correct Answer	Incorrect Answer	Not Attempted	Total Marks