G-66

**Invigilator's Signature**

# ENTRANCE EXAMINATION – 2014
## Ph. D. Chemistry

**TIME: 2 HOURS** **MAXIMUM MARKS: 75**

**HALL TICKET NUMBER:** | |

## INSTRUCTIONS

1. Write your **HALL TICKET NUMBER** in the space provided above and also in the **OMR** ANSWER SHEET given to you.
2. Make sure that pages numbered from **1 - 13** (excluding 3 pages assigned for rough work) are present.
3. There are 55 (Fifty five) multiple choice questions in this paper (15 in Part A + 40 in Part B). You are required to answer all questions of Part A and maximum 15 questions from Part B. If more than the required numbers of questions are answered, only the first 15 questions of Part B, will be taken up for evaluation.
4. Each question of Part A carries **ONE** mark only, whereas each question of Part B carries **FOUR** marks.
4. **There is negative marking. Each wrong answer in Part A carries -0.33 mark and in Part B carries -1.32 marks.**
5. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
6. Hand over the OMR answer sheet at the end of the examination to the Invigilator.
7. In case of a tie, the marks obtained in the first 15 questions (**PART A**) will be used to determine the order of merit.
8. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
9. Calculators are allowed. Cell phones are not allowed.
10. Useful constants are provided at the beginning of PART A in the question paper.
11. OMRs without hall ticket number will not be evaluated and University shall not be held responsible.

**Useful Constants:**

Rydberg constant = 109737 $cm^{-1}$; Faraday constant = 96500 C; Planck constant = $6.625 \times 10^{-34}$ J s; Speed of light = $2.998 \times 10^{8}$ m $s^{-1}$; Boltzmann constant = $1.380 \times 10^{-23}$ J $K^{-1}$; Gas constant = 8.314 J $K^{-1}$ $mol^{-1}$; Mass of electron = $9.109 \times 10^{-31}$ kg; Mass of proton = $1.672 \times 10^{-27}$ kg; Charge of electron = $1.6 \times 10^{-19}$ C; 1 D = $3.336 \times 10^{-30}$ Cm; 1 bar = $10^{5}$ $Nm^{-2}$; RT/F (at 298.15 K) = 0.0257 V; 1 kcal/mol = 350 $cm^{-1}$.

# Part A

1. The well-behaved function of $x$ ($-\infty \leq x \leq +\infty$) among the following is

(A) $1/x$ (B) $e^{-ax^2}$ (C) $e^{(-a|x|)}$ (D) $1/|x|^{1/4}$

2. Methanol can be produced by the following exothermic process:

$$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$$

The conditions necessary to maximize the equilibrium yield of $CH_3OH$ are

(A) Low temperature and low pressure
(B) High temperature and low pressure
(C) Low temperature and high pressure
(D) High temperature and high pressure

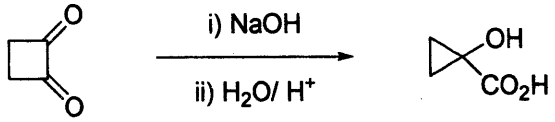
3. An achiral molecule has no centre of inversion. To which point group does it belong?

(A) $C_2$ (B) $C_{2v}$ (C) $D_{2h}$ (D) $D_2$

4. A hydrogen atomic orbital that has two radial nodes and three angular nodes is

(A) $2p$ (B) $3d$ (C) $5g$ (D) $6f$

5. The following reaction involves

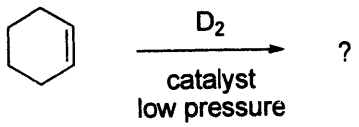



(A) Wolf Rearrangement (B) Benzylic acid Rearrangement
(C) Steven's Rearrangement (D) Wagner-Meerwin Rearrangement

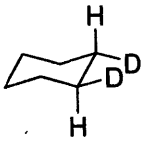
6. "Ring current effect" is related to

(A) NMR (B) ESR (C) IR (D) MS

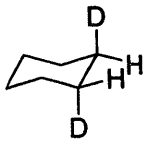
7. The major product obtained in the following reaction is



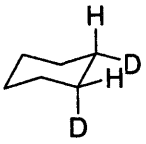

(A)




(B)




(C)

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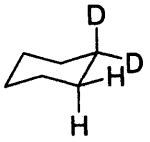
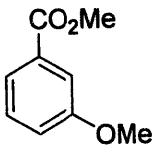



8. The ester which undergoes acid hydrolysis faster is

(A)

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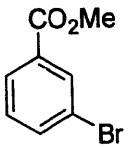


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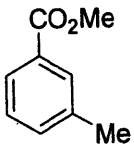


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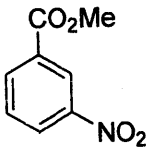
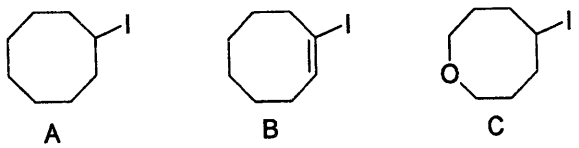



9. The order of relative rate of solvolysis among the iodides A-C is




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

10. How many moles of sulfuric acid can be produced from four moles of iron pyrite ($FeS_2$) on treatment with oxygen and then water (assuming no loss)?

(A) 4 (B) 8 (C) 6 (D) 2

11. The electrically conducting material among the following is

(A) Diamond (B) Fullerene (C) $(SN)_x$ polymer (D) $S_4N_4$

12. The reaction of $[Pt(NH_3)_4]^{2+}$ with two equivalents of chloride ions will produce:

(A) *Trans*-$[Pt(NH_3)_2Cl_2]$
(B) *Cis*-$[Pt(NH_3)_2Cl_2]$
(C) *Trans*-$[Pt(NH_3)_4Cl_2]$
(D) Mixture of *cis*-$[Pt(NH_3)_2Cl_2]$ and *trans*-$[Pt(NH_3)_2Cl_2]$

13. Relation between the crystal field splitting in a cubic geometry ($\Delta_c$) and octahedral geometry ($\Delta_o$) is

(A) $\Delta_c = 4/3\Delta_o$ (B) $\Delta_c = 4/9\Delta_o$ (C) $\Delta_c = 8/6\Delta_o$ (D) $\Delta_c = 8/9\Delta_o$

14. Ribosome is the site of

(A) DNA synthesis (B) DNA methylation
(C) Protein synthesis (D) RNA synthesis

15. Which of the following structure types is associated with inter-subunit contacts in multimeric proteins?

(A) Primary structure (B) Secondary structure
(C) Tertiary structure (D) Quaternary structure

**End of Part A**

# Part B

16. The shapes of $IF_5$, $XeF_4$ and $Ni(CN)_4^{2-}$ are, respectively,

(A) Square pyramid, square planar and tetrahedral
(B) Trigonal bipyramid, tetrahedral and square planar
(C) Square pyramid, square planar and square planar
(D) Trigonal bipyramid, square planar and tetrahedral

17. The number of B-H-B and B-B bonds in $B_4H_{10}$ respectively, are

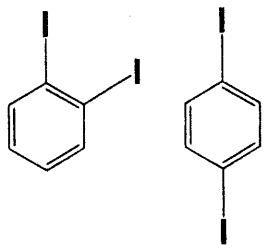
(A) Four and two (B) Two and four
(C) Three and two (D) Four and one

18. In each set (i) to (iv), below identify the species which matches the property mentioned against the set

(i) Cl, Si, K : lowest ionization energy
(ii) $CO_2$, $NH_3$, CO : zero dipole moment
(iii) $CH_4$, $NH_3$, HF : highest boiling point
(iv) HOI, HOBr, HOCl : weakest acid

(A) (i) Cl, (ii) $CO_2$, (iii) HF, (iv) HOI (B) (i) K, (ii) CO, (iii) HF, (iv) HOCl
(C) (i) K, (ii) $CO_2$, (iii) HF, (iv) HOI (D) (i) K, (ii) $CO_2$, (iii) $NH_3$, (iv) HOCl

19. Assuming that (i) C-I distance is 2.1 Å, (ii) carbon to carbon distance is 1.4 Å, (iii) all C-C distances are equal and (iv) the six membered ring is perfectly hexagonal, the correct distance between the centers of the two iodine atoms in the following two molecules, respectively are



(A) 3.5 and 7.0 Å (B) 3.5 and 5.6 Å
(C) 4.2 and 7.0 Å (D) 4.2 and 5.6 Å

20. Energies of the d-orbitals in a trigonal bipyramidal crystal field are in the order:

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

21. In the gravimetric estimation of nickel, 0.56 g of $[Ni(HDMG)_2]$ was obtained from 0.35 g of an nickel containing alloy. The percentage of nickel (At. wt. 58.69) in the alloy is

(A) 20.0 (B) 55.5 (C) 81.4 (D) 32.5

22. The ground state Russell-Saunders term symbol for $Nd^{3+}$ ion is

(A) $^4I_{9/2}$ (B) $^1S_0$ (C) $^7F_0$ (D) $^2F_{7/2}$

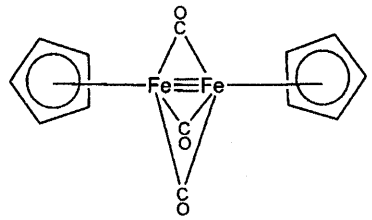
23. The experimental hydration energies of $Ca^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ were plotted against atomic numbers. A straight line passing through these points gave a value of −716 kcal/mol as the hydration energy of $Ni^{2+}$. If the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition for $[Ni(H_2O)_6]^{2+}$ occurs at 8650 $cm^{-1}$, calculate the expected hydration energy (in kcal/mol) of $Ni^{2+}$ ?

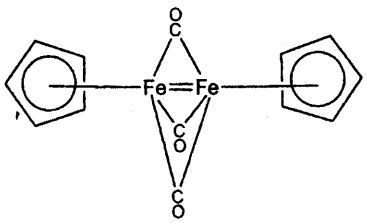
(A) −666 (B) −686 (C) −746 (D) −766

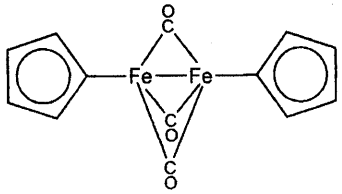
24. The molecular structure of $S_2O_3^{2-}$ is

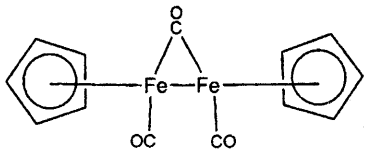
(A) A dimeric one with S-S bond
(B) A dimeric one with S=S bond
(C) Trigonal planar
(D) Tetrahedral

25. Photolysis of $[\eta^5\text{-CpFe(CO)}_2]_2$ at -78°C results in the loss of a colorless gas and formation of an iron containing compound, having a single carbonyl band at 1785 $cm^{-1}$ in IR spectrum and 14.7 % oxygen by mass. Choose the product from the following:

(A) 


(B) 


(C) 


(D) 


26. Using total valence electron counting and polyhedral electron counting, the structures of $Os_5(CO)_{16}$ and $Os_5(CO)_{15}C$, respectively are

(A) Closo and nido
(B) Closo and arachno
(C) Nido and arachno
(D) Nido and closo

27. Match the followings:

| | | | |
|---|---|---|---|
| 1 | $Ti(BH_4)_3(PMe_3)_2$ | a | Wilkinson's catalyst |
| 2 | 1-Octene → Octane | b | *Oxo* process |
| 3 | Butyraldehyde | c | Monsanto process |
| 4 | Acetic acid | d | Agostic interaction |

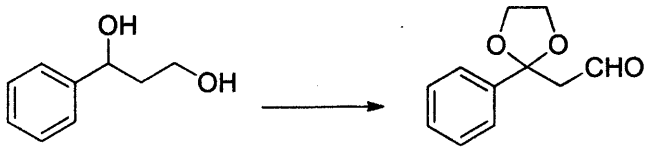
(A) 1 = c; 2 = a; 3 = b; 4 = d
(B) 1 = b; 2 = a; 3 = c; 4 = d
(C) 1 = a; 2 = b; 3 = c; 4 = d
(D) 1 = d; 2 = a; 3 = b; 4 = c

28. Match the followings:

| | | | |
|---|---|---|---|
| 1 | Hemoglobin | a | Electron transfer |
| 2 | Vitamin $B_{12}$ | b | Active site is a Zn-complex |
| 3 | Carboxypeptidase | c | Oxygen transport |
| 4 | Ferredoxin | d | Active site is a Co-complex |

(A) 1 = c; 2 = d; 3 = b; 4 = a
(B) 1 = c; 2 = b; 3 = d; 4 = a
(C) 1 = c; 2 = d; 3 = a; 4 = b
(D) 1 = a; 2 = d; 3 = b; 4 = c

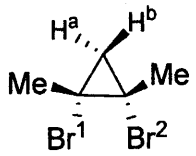
29. The appropriate three step sequence required for the conversion of A to B is




A B

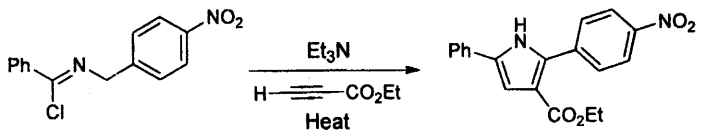
| | |
|---|---|
| (A) $MnO_2$; $(CH_2OH)_2$/ *p*-TSA; PCC | (B) PCC; $MnO_2$; $(CH_2OH)_2$/ *p*-TSA |
| (C) PCC; $(CH_2OH)_2$/ *p*-TSA; Jone's reagent | (D) Jone's reagent; $MnO_2$; $(CH_2OH)_2$/ *p*-TSA |

30. The relation between the $H^a$ and $H^b$ and $Br^1$ and $Br^2$ in the given compound is




| | |
|---|---|
| (A) $H^a$, $H^b$ are enantiotopic; and $Br^1$, $Br^2$ are diastereotopic | (B) $H^a$, $H^b$ are diastereotopic; and $Br^1$, $Br^2$ are enantiotopic |
| (C) $H^a$, $H^b$ are diastereotopic; and $Br^1$, $Br^2$ are homotopic | (D) $H^a$, $H^b$ are enantiotopic; and $Br^1$, $Br^2$ are homotopic |

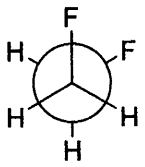
31. The following conversion involves

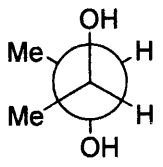



| | |
|---|---|
| (A) A 1,3-diolar species as reactive intermediate followed by Aza-Wittig reaction | (B) A carbenium ion as reactive intermediate, followed by Aza-Cope rearrangement |
| (C) A 1,3-diolar species as reactive intermediate, followed by cycloaddition | (D) A carbenium ion as reactive intermediate, followed by cycloaddition |

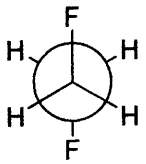
32. The most stable conformations of 1,2-difluoroethane and *dl*-2,3-butanediol are

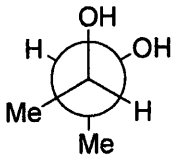
(A)




(B)

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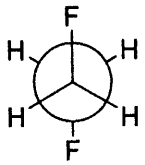
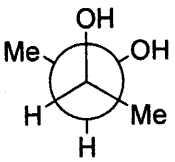
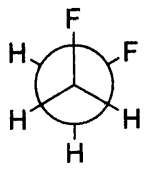
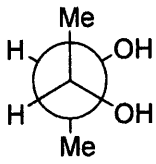


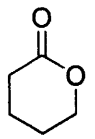




(D)

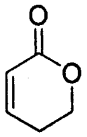


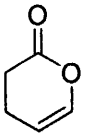

33. Arrange the following compounds in decreasing order of IR stretching frequency of C=O



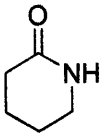

i




ii




iii




iv

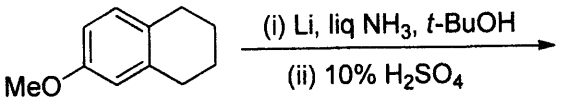
(A) i > ii > iii > iv

(B) iii > i > ii > iv

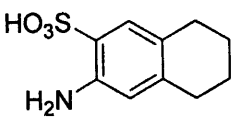
(C) ii > i > iii > iv

(D) iv > i > ii > iii

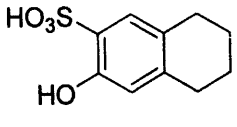
34. The major product obtained in the following reaction is



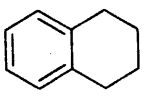

(A)



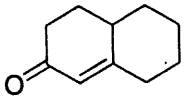

(B)



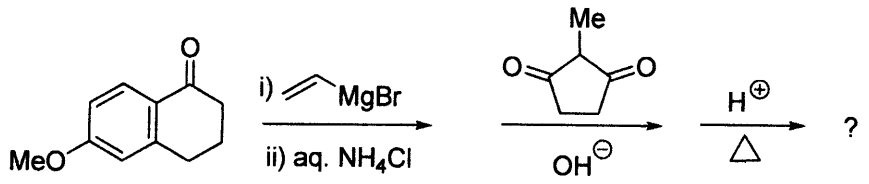

(C)



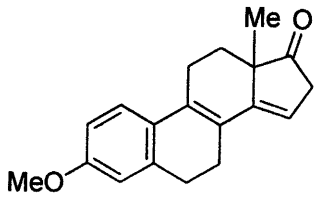
(D)



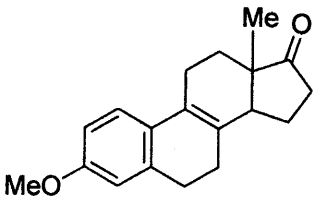
35. The product obtained in the following transformation is



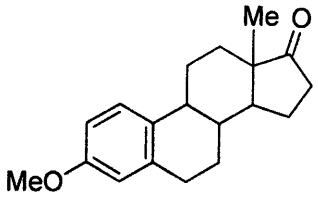

(A)



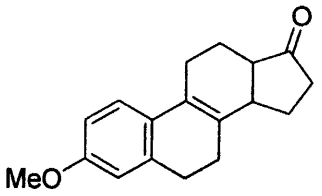

(B)



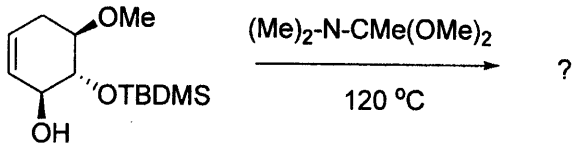

(C)



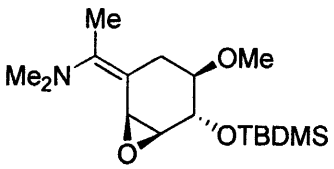

(D)



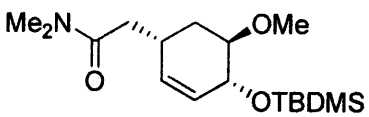

36. The major product obtained in the following reaction is



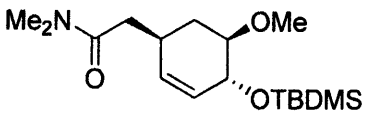

(A)



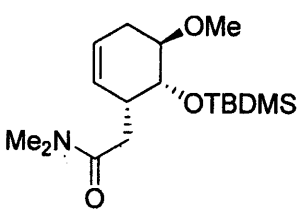

(B)



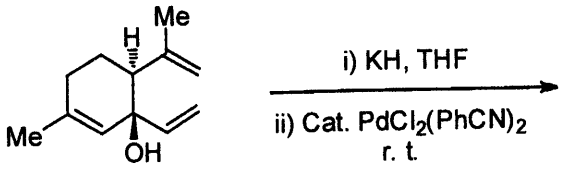

(C)



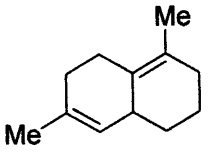

(D)



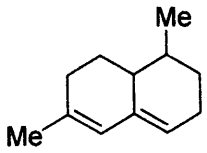
37. The major product obtained in the following reaction is



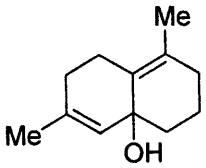

(A)



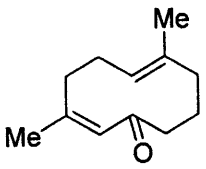

(B)




(C)

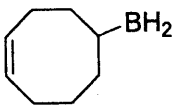



(D)

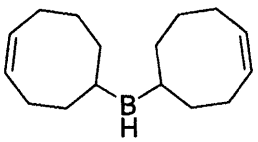



38. The major product obtained in the reaction between 1,5-cyclooctadiene and diborane (0.5 equivalents) is

(A)

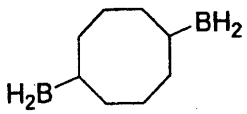



(B)

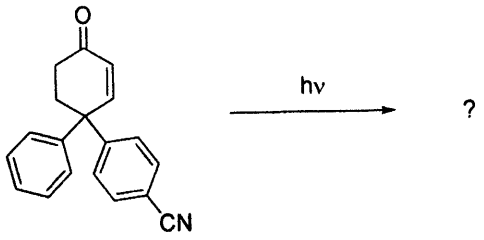



(C)

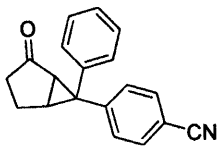

(D)



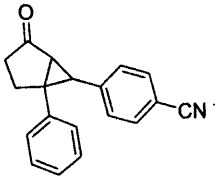

39. The major product obtained in the following photochemical reaction is



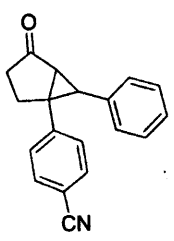

(A)



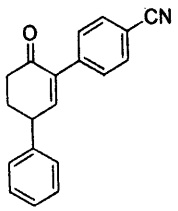

(B)



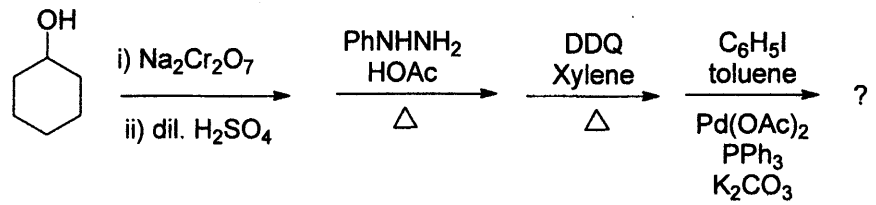

(C)



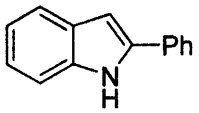

(D)



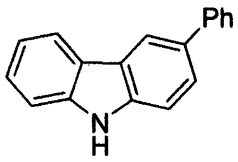
40. Identify the product in the following transformation



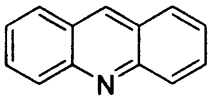

(A)



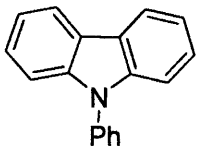

(B)




(C)



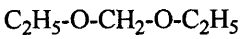

(D)



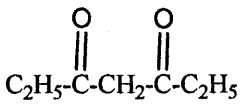

41. The compound showing the following spectral characteristic is

$^1$H NMR ($\delta$ in ppm) = 4.65 (2H, singlet), 3.65 (4H, quartet), 1.25 (6H, triplet); $^{13}$C NMR ($\delta$ in ppm) = 15, 63, 95; DEPT-135 ($\delta$ in ppm) = 15 (positive), 63 (negative), 95 (negative); DEPT-90 ($\delta$ in ppm) = 15 (no peak), 63 (no peak), 95 (no peak).

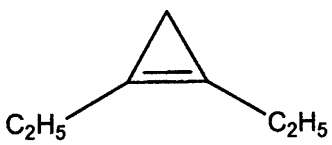
(A)



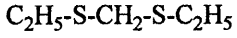

(B)




(C)




(D)




42. A solution (0.5 g/mL) of penicillin-V shows the optical rotation of +220° in 20 cm cell. The specific rotation of penicillin-V is +330°. The optical purity of penicillin-V in this solution is

(A) 78.6 (B) 66.6 (C) 33.4 (D) 88.6

43. If the F-F bond enthalpy is +155 kJ $mol^{-1}$ and the electron gain enthalpy (electron affinity) of fluorine atom is -328 kJ $mol^{-1}$, which of the following represents the standard enthalpy change (in kJ $mol^{-1}$) for the reaction

$$F_2\,(g) + 2\,e^-\,(g) \rightarrow 2\,F^-\,(g)$$

(A) -18 (B) -173 (C) -501 (D) -811

44. The rate constant for the following substitution reaction increases by a factor of 10.6 when the temperature is increased from 298 K to 308 K. The activation energy of the reaction in kJ $mol^{-1}$ is

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

(A) 180 (B) 78.2 (C) 809 (D) 2.14

45. Adsorption of a gas is described by the Langmuir isotherm with K = 0.75 $kPa^{-1}$ at 25°C. The pressure (in kPa) at which the fractional surface coverage becomes 0.25 is

(A) 0.158 (B) 0.44 (C) 0.265 (D) 0.33

46. At 25°C, the density of mercury is 13.53 $g/cm^3$ and surface tension is 0.484 N/m. The amount of capillary depression (in m) of mercury in a glass tube of 1 mm inner diameter would be (assume the contact angle $\theta = 180^\circ$ and the density of air is negligible)

(A) 0.0146 (B) 0.0073 (C) 1.46 (D) 0

47. Vapour pressure, $p$ (Torr) of a liquid is found to vary with the temperature, $T$ (K), following the expression $\log(p) = 7.96 - 1780/T$ within a temperature range of interest. The normal boiling point (in K) and enthalpy of vaporization (in kJ/mol) of the liquid respectively are

(A) 178.0; 7.960 (B) 350.4; 34.08 (C) 351.0; 14.80 (D) 178.0; 34.08

48. If in an X-ray diffraction experiment, the peak for the (111) plane of a cubic lattice is observed at $2\theta = 25.0^\circ$, than the peak for the (230) plane will appear at a $2\theta$ value of

(A) 108.0° (B) 61.6° (C) 53.6° (D) 26.8°

49. The standard electrode potentials for $Cu^{2+}(aq)/Cu(s)$ and $Cu^{+}(aq)/Cu(s)$ are +0.34 V and +0.52 V, respectively. The equilibrium constant for the reaction: $2Cu^{+}\,(aq) \rightarrow Cu^{2+}\,(aq) + Cu\,(s)$ at 25°C is

(A) $6.8 \times 10^{11}$ (B) $1.2 \times 10^{6}$ (C) $1.1 \times 10^{3}$ (D) 1.0

50. The average value of $x$, $\langle x \rangle$, in the ground state of a particle in a box of length $l$ where $0 \leq x \leq l$ is

(A) $l/2$ (B) $l$ (C) $l/4$ (D) $2l$

51. The rotational transition from $J = 3$ to $J = 4$ for a diatomic molecule occurs at $\lambda = 2.0$ cm. The $\lambda$ (in cm) for the transition from $J = 5$ to $J = 6$ for this molecule would be

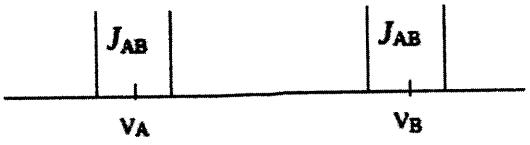
(A) 2.85 (B) 1.14 (C) 1.33 (D) 3.33

52. A spectroscopic technique that can give information on the bonding characteristics of a single orbital is

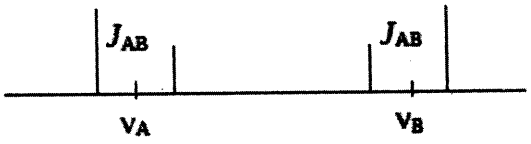
(A) UV-Vis (B) NMR (C) EPR (D) Photoelectron

53. Among the following schematic spectra, the NMR spectrum of an AB spin system is

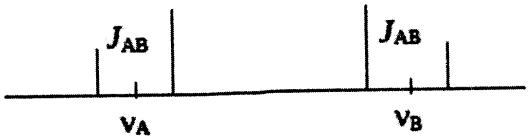
(A)



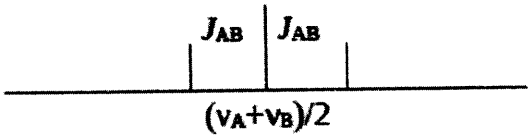

(B)




(C)




(D)




54. The distribution of errors in age for a group of students is given by the following Gaussian form:

$$f(x) = \sqrt{(A/\pi)}\, e^{-Ax^2}$$

The average and the standard deviation, respectively, for this distribution are

(A) $\langle x \rangle \neq 0$ and $\sigma_x = 1/\sqrt{A}$ (B) $\langle x \rangle = 0$ and $\sigma_x = 1/\sqrt{2A}$

(C) $\langle x \rangle = 0$ and $\sigma_x = \sqrt{A}$ (D) $\langle x \rangle \neq 0$ and $\sigma_x = A$

55. The half-life of $^{32}P$ is 14.3 days. If the specific activity of a sample of [$^{32}P$] ATP on January 13, 2014 was 5.3 Ci/mmol, the specific activity (in Ci/mmol) on February 08, 2014 would be

(A) 5.3 (B) 2.98 (C) 0.75 (D) 1.49

**End of Part B**