M-55

ENTRANCE EXAMINATION-2016

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 20 questions from Part-B***. If more than the required numbers of questions are answered **only the first 20 questions of Part-B** will be taken up for evaluation.
4. Each questions of Part-A carries **ONE (01)** mark only, whereas each question of Part-B carries **THREE (03)** marks.
5. ***There is negative marking. Each wrong answer in Part-A carries -0.33 mark and in Part-B carries -1.00 marks.***
6. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
7. Hand over the OMR answer sheet at the end of the examination to the Invigilator.
8. In case of a tie, the marks obtained in **the first 15 questions** (**PART-A)** will be used to determine the order of merit.
9. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
10. Calculators are allowed. Cell phones are not allowed.
11. Useful constants are provided at the beginning of PART-A in the question paper.
12. *OMRs without hall ticket number will not be evaluated and University shall not be held responsible.*

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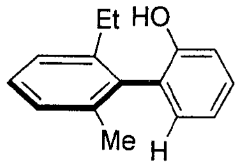
Useful constants:

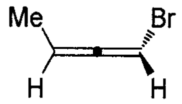
Rydberg constant = 109737 cm^{-1}; Faraday constant = 96500 C; Plank constant = 6.625×10^{-34} J s; Speed of light = 2.998×10^{8} m s^{-1}; Boltzmann constant = 1.380×10^{-23}J K^{-1}; Gas constant = 8.314 J K^{-1} mol^{-1} = 1.987 cal K^{-1} mol^{-1}; Mass of electron = 9.109×10^{-31} kg; Mass of proton = 1.672×10^{-27} kg;Charge of electron = 1.6×10^{-19} C; 1 D = 3.336×10^{-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 absolute configurations of the following compounds **X** and **Y**, respectively, are.



X

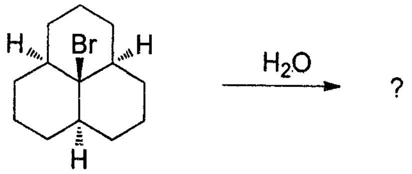


Y

(A) *R, S* (B) *S, R*

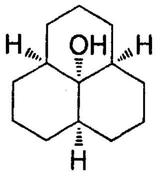
(C) *R, R* (D) *S, S*

2. Predict the product and the way it is formed (S_N1 or S_N2) in the following reaction.



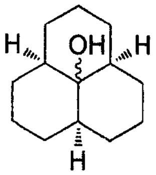
(A)

S_N2



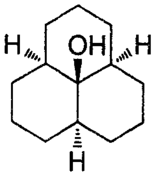
(B)

S_N1



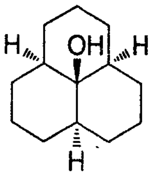
(C)

S_N2



(D)

S_N1



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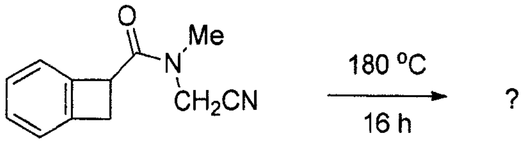
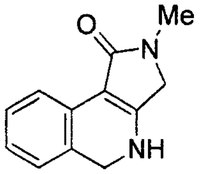
3. Find the product obtained in the following transformation.



(A)



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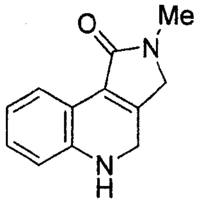

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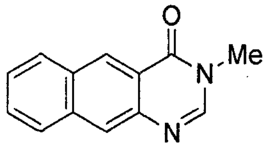

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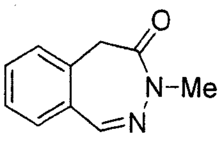
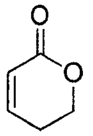
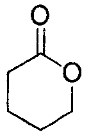


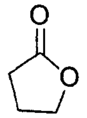
4. Find the order of carbonyl stretching frequencies in IR spectra of the following compounds.



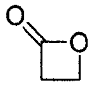
(I)



(II)



(III)



(IV)

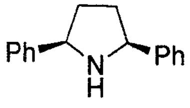
(A) (I) > (II) > (III) > (IV)

(B) (IV) > (III) > (I) > (II)

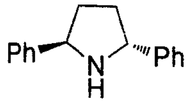
(C) (IV) > (III) > (II) > (I)

(D) (I) > (IV) > (III) > (II)

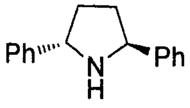
5. Identify the following compounds.



I



II



III

(A) I = (2R,5S)-2,5-diphenylpyrrolidine
II = (2S,5S)-2,5-diphenylpyrrolidine
III = (2R,5R)-2,5-diphenylpyrrolidine

(B) I = (2S,5R)-2,5-diphenylpyrrolidine
II = (2S,5S)-2,5-diphenylpyrrolidine
III = (2S,5R)-2,5-diphenylpyrrolidine

(C) I = (2R,5R)-2,5-diphenylpyrrolidine
II = (2R,5R)-2,5-diphenylpyrrolidine
III = (2S,5R)-2,5-diphenylpyrrolidine

(D) I = (2S,5R)-2,5-diphenylpyrrolidine
II = (2R,5R)-2,5-diphenylpyrrolidine
III = (2S,5S)-2,5-diphenylpyrrolidine

6. The molecular shapes of IF_5 and $[XeF_5]^-$ are, respectively,

(A) Trigonal bipyramidal and trigonal bipyramidal

(B) Square pyramidal and pentagonal planar

(C) Trigonal bipyramidal and pentagonal planar

(D) Square pyramidal and square pyramidal

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7. The half life of a radioactive nucleus 'X' is 1.386 h. How many moles of 'X' will remain after 4.606 h if the initial quantity is 0.1 mole?

(A) 0.030	(B) 0.002
(C) 0.001	(D) 0.010

8. The numbers of faces, edges and vertices in a bicapped square-antiprism are

(A) 18, 27 and 12, respectively	(B) 16, 24 and 10, respectively
(C) 14, 21 and 8, respectively	(D) 12, 18 and 6, respectively

9. The active site of metalloprotein oxyhemocyanin contains

(A) Co(II) and O_2^{2-}	(B) Cu(II) and O_2^{2-}
(C) Co(IV) and O_2^{-}	(D) Fe(III) and O_2^{2-}

10. The total number of metal-metal bonds in $Ir_4(CO)_{12}$ is

(A) Zero	(B) Four
(C) Six	(D) Eight

11. Which of the following is not true about diamagnetic susceptibility?

(A) Decreases exponentially with increasing temperature	(B) Value is negative
(C) An important characteristic of superconductors	(D) Relatively weak compared to paramagnetic susceptibility

12. The molar residual entropy of 1,2-difluorobenzene in the crystalline state is

(A) $R \ln 6$	(B) 0
(C) $R \ln 2$	(D) $3R \ln 2$

13. For a first order reaction with stoichiometric equation, 2A →Products, ln[A] at time t is related to $\ln[A]_0$ as: (k is the rate constant for the formation of product)

(A) $\ln[A] = -2kt + \ln[A]_0$	(B) $\ln[A]_0 = -2kt + \ln[A]$
(C) $\ln[A]_0 = -2kt - \ln[A]$	(D) $\ln[A] = -kt + 2\ln[A]_0$

14. Which one of the following is not a crystallographic point group?

(A) T_h	(B) D_{8d}
(C) C_s	(D) D_{6h}

15. The number of fundamental bands that can be seen in the IR spectrum of CO_2 is

(A) 1	(B) 2
(C) 3	(D) 4

--**End of Part A**--

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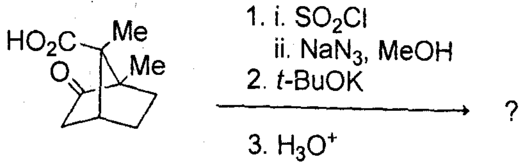
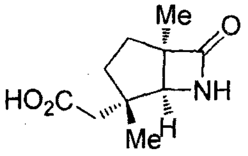
Part-B

16. The major product formed in the following reaction sequences is



(A)



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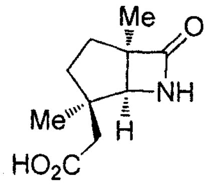
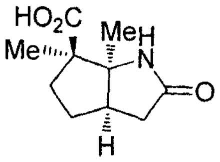


(C)



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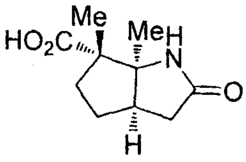
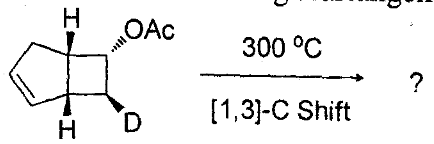
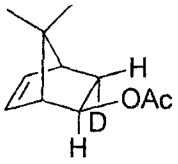


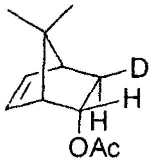
17. Find the major product obtained in the following rearrangement



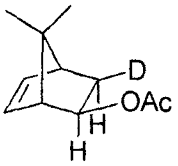
(A)



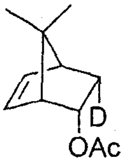
(B)



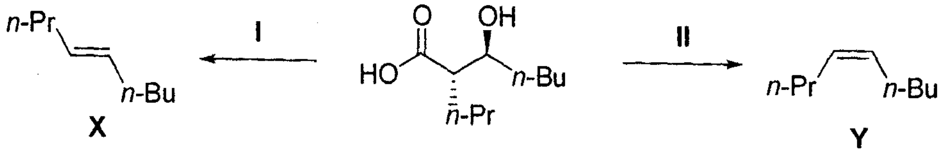
(C)



(D)



18. Suggest the reagents I and II required for the formation of following products **X** and **Y**, respectively



(A) I = pyridine, $MeSO_2Cl$, 100 °C;
II = p-TSA, MeOH, 100 °C

(B) I = Ph_3P, $EtO_2C\text{-}N\text{=}N\text{-}CO_2Et$;
II = pyridine, $MeSO_2Cl$, 100 °C

(C) I = pyridine, $MeSO_2Cl$, 100 °C;
II = Ph_3P, $EtO_2C\text{-}N\text{=}N\text{-}CO_2Et$

(D) I = Ph_3P, $EtO_2C\text{-}N\text{=}N\text{-}CO_2Et$;
II = p-TSA, MeOH, 100 °C

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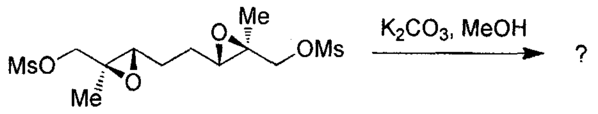
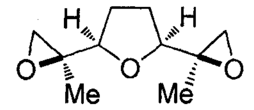
19. Find the product in the following reaction.



(A)



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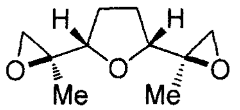
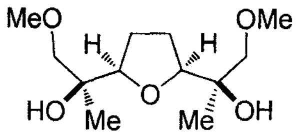
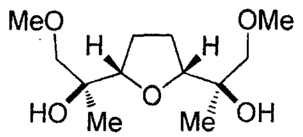


(C)

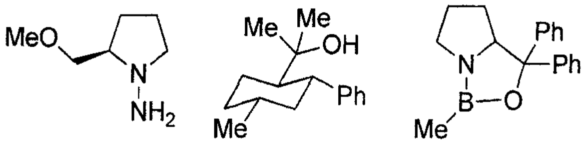


(D)

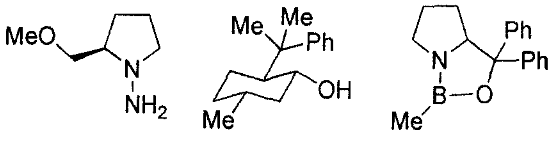


20. Find the structure of RAMP, 8-phenylmenthol and Corey-Bakshi-Shibata (CBS) reagents among the following choices.

(A)



(B)



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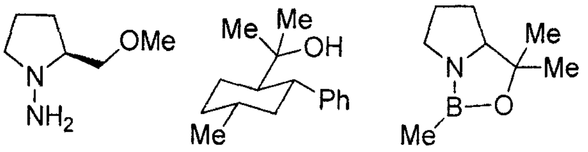

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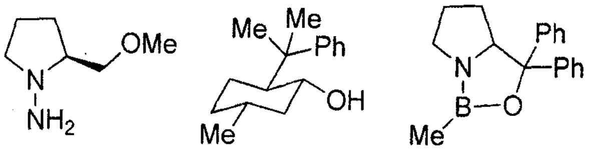
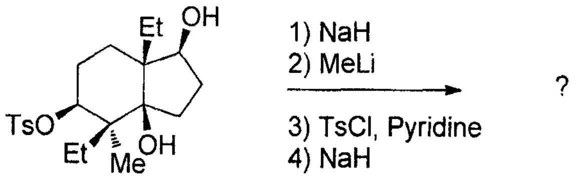
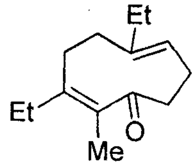


21. The major product obtained in the following transformation is



(A)



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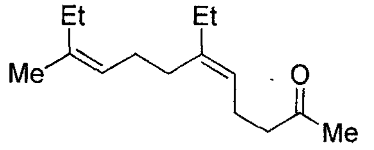

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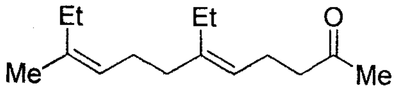

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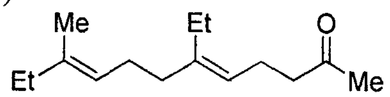

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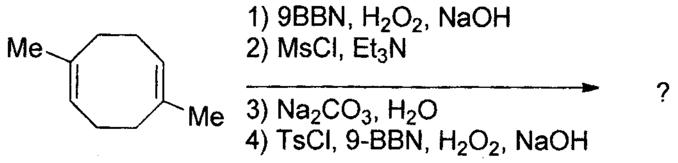
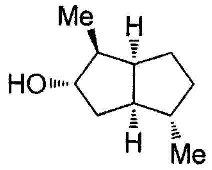
22. Find the product obtained in the following reaction.



(A)



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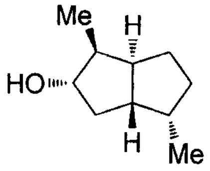
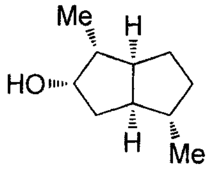


(C)



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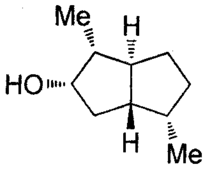
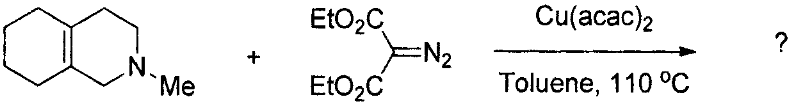
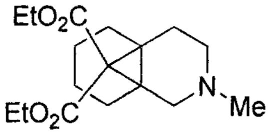


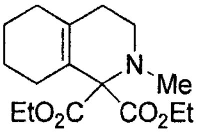
23. The major product obtained in the following transformation is



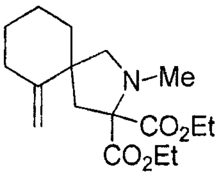
(A)



(B)



(C)



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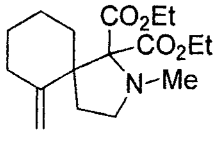
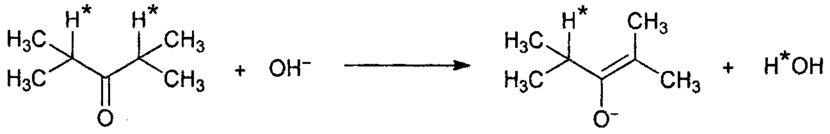
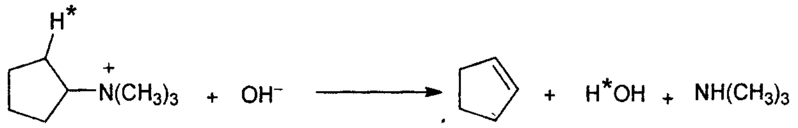


24. Indicate the kinetic isotopic effect for the following transformations.



(I)



(II)

(III)

(A) I Primary, II Secondary, III Primary
(B) I Primary, II Primary, III Secondary
(C) I Secondary, II Primary, III Secondary
(D) I Secondary, II Secondary, III Primary

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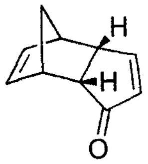
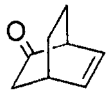
25. Match the compounds in the column **I** with the photochemical reaction that they can undergo given in the column **II**.

I

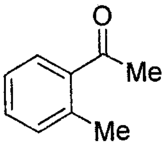
(i)



(ii)



(iii)

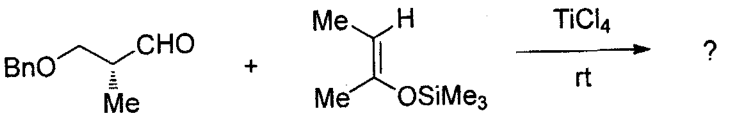


II

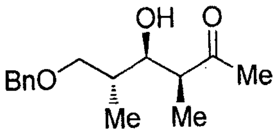
(p) oxa di-π-methane rearrangement
(q) Paterno-Buchi reaction
(r) intramolecular [2+2] cycloaddition
(s) photoenolisation

(A) (i)-(q); (ii)-(s); (iii)-(p)
(B) (i)-(r); (ii)-(p); (iii)-(s)
(C) (i)-(p); (ii)-(r); (iii)-(q)
(D) (i)-(r); (ii)-(q); (iii)-(s)

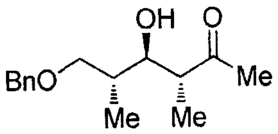
26. Predict the most probable product obtained in the following transformation.



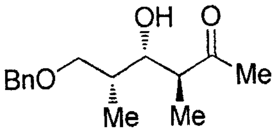
(A)



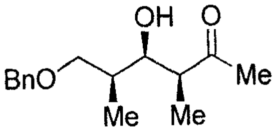
(B)



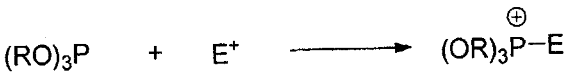
(C)



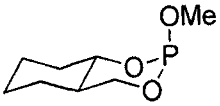
(D)



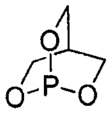
27. Rank the reactivity of phosphites in the following transformation.



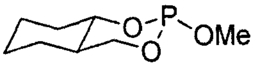
$$(RO)_3P \quad + \quad E^+ \longrightarrow (OR)_3\overset{\oplus}{P}{-}E$$



I



II



III

(A) I > II > III
(B) III > I > II
(C) II > I > III
(D) III > II > I

28. The spectral data of an unknown compound show the following **representative** peaks.

IR: a broad peak from 2500-3500 cm^{-1}, a peak at 1680 cm^{-1}.

^{13}C NMR: shows four peaks in the region 125-145 ppm in addition to other peaks.

Mass: 136 (M), 119, 91, 65, 39.

The structure of the compound is

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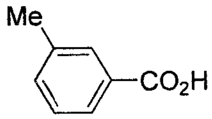
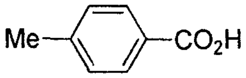
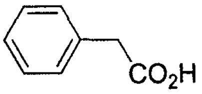
(A)



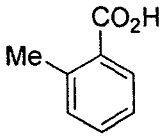
(B)



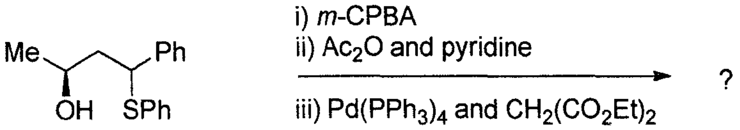
(C)



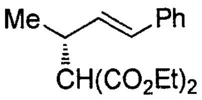
(D)



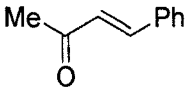
29. Identify the most probable product obtained in the following transformation.



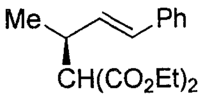
(A)



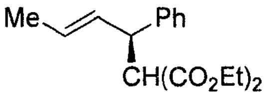
(B)



(C)



(D)



30. Based on the equation, $pK_a = 15.1-(88.2Z^2/r)$ {Z = charge on the cation}, the relative acidities of Eu^{2+} ($Z^2/r = 0.03$), Ti^{4+} ($Z^2/r = 0.20$) and Mg^{2+} ($Z^2/r = 0.05$) are expected to be in the order:

(A) $Eu^{2+} < Mg^{2+} < Ti^{4+}$
(B) $Eu^{2+} > Mg^{2+} > Ti^{4+}$
(C) $Mg^{2+} < Eu^{2+} < Ti^{4+}$
(D) $Mg^{2+} > Eu^{2+} > Ti^{4+}$

31. The E° values for $Ag^+ + e \rightleftharpoons Ag$ and $Cu^{2+} + 2e \rightleftharpoons Cu$ are 0.80 and 0.34 V, respectively. If a piece of copper is added to a 0.05 M aqueous solution of $AgNO_3$, the equilibrium composition of the solution will be

(A) $[Cu^{2+}] = 0.025$ M and
$[Ag^+] = 2.53 \times 10^{-9}$ M

(B) $[Cu^{2+}] = 0.05$ M and
$[Ag^+] = 0.025$ M.

(C) $[Cu^{2+}] = 2.53 \times 10^{-9}$ M and
$[Ag^+] = 0.025$ M

(D) $[Cu^{2+}] = 0.025$ M and
$[Ag^+] = 2.53 \times 10^{-18}$ M

32. The magnitudes of the crystal field splitting (Δ_o) and the mean pairing energy (P) for $[Cr(H_2O)_6]^{2+}$ are 13900 and 23500 cm^{-1}, respectively. The CFSE values for the high-spin and the low-spin states of $[Cr(H_2O)_6]^{2+}$ are

(A) 8340 and −1260 cm^{-1}, respectively
(B) −1390 and 2350 cm^{-1}, respectively

(C) −8340 and 1260 cm^{-1}, respectively
(D) 1390 and −2350 cm^{-1}, respectively

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33. An octahedral complex of formula $[M(AB)(CD)E_2]$ (AB and CD are unsymmetrical bidentate ligands and E is a monodentate ligand) can have

(A) 3 geometrical isomers and 1 of them will be optically active

(B) 4 geometrical isomers and 2 of them will be optically active

(C) 5 geometrical isomers and 3 of them will be optically active

(D) 6 geometrical isomers and 4 of them will be optically active

34. The electronic spectrum of $[CrF_6]^{3-}$ displays three bands at 14900, 22700 and 34400 cm^{-1}. The crystal field splitting energy (Δ_o), crystal field stabilization energy (CFSE), Racah parameter (B′) and the Nephelauxetic ratio (β) [Racah parameter B for free Cr^{3+} is 918 cm^{-1}] are

(A) $\Delta_o = 17880\ cm^{-1}$, CFSE = $14900 cm^{-1}$, $B' = 872\ cm^{-1}$ and $\beta = 0.95$

(B) $\Delta_o = 14900\ cm^{-1}$, CFSE = $17880 cm^{-1}$, $B' = 827\ cm^{-1}$ and $\beta = 0.90$

(C) $\Delta_o = 22700\ cm^{-1}$, CFSE = $14900 cm^{-1}$, $B' = 782\ cm^{-1}$ and $\beta = 0.85$

(D) $\Delta_o = 19500\ cm^{-1}$, CFSE = $11700 cm^{-1}$, $B' = 728\ cm^{-1}$ and $\beta = 0.79$

35. The infrared spectrum of free Me_2SO displays the S=O stretch at 1055 cm^{-1}. In comparison, $[Mn(OSMe_2)_6](ClO_4)_3$ shows two S=O stretches at 915 and 960 cm^{-1} in its infrared spectrum. The intensity of 915 cm^{-1} band is almost double of the intensity of 960 cm^{-1} band. The order of the d-orbitals with respect to the corresponding energies and the electron distribution in them for the metal center in $[Mn(OSMe_2)_6](ClO_4)_3$ is

(A) $d_{xz}^1, d_{yz}^1 < d_{xy}^1 < d_{z2}^1 < d_{x2-y2}$

(B) $d_{xz}^1, d_{yz}^1 < d_{xy}^1 < d_{z2} < d_{x2-y2}$

(C) $d_{xy}^1 < d_{xz}^1, d_{yz}^1 < d_{x2-y2}^1 < d_{z2}$

(D) $d_{xy}^1, d_{xz}^1, d_{yz}^1 < d_{x2-y2}^1, d_{z2}$

36. The number of microstates and the ground term symbol for Ni^{3+} are

(A) 45 and $^3F_4$, respectively

(B) 120 and $^4F_{3/2}$, respectively

(C) 120 and $^4F_{9/2}$, respectively

(D) 45 and $^3F_2$, respectively

37. The metal centers in the metalloenzymes involved in the following conversions are

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$
$R\text{-}CO\text{-}NH\text{-}CHR'\text{-}COO^- + H_2O \rightarrow RCOO^- + H_3N^+\text{-}CHR'\text{-}COO^-$
$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(A) nickel, copper, zinc and manganese, respectively

(B) tungsten, manganese, molybdenum and tungsten, respectively

(C) molybdenum, zinc, tungsten, and manganese, respectively

(D) manganese, tungsten, iron and magnesium, respectively

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38. Iron storage proteins are known as metalloproteins **W**, built up of a hollow protein sphere (molecular weight = 450 kDa) consisting of **X** subunits of 163 amino acids each with an outer diameter of 130 and an inner diameter of 70 Å. The inner surface of this capsule is lined with carboxylate functions, which can coordinate Fe^{3+}. A maximum number **Y** of Fe^{3+} can be accommodated inside this hollow protein capsule. Various iron centers are connected by bridging oxido and hydroxido groups very much as in the colloidal form of ferric hydroxide. The overall composition of the iron nucleus is **Z**. **W**, **X** and **Y** and **Z** are

(A) Siderophores, 56, 100000, and $4Fe_2O_3{\cdot}Fe_2(SO_4)_3$, respectively

(B) Ferritins, 8, 4000, and $9Fe_3O_4{\cdot}FeO(H_2PO_4)$, respectively

(C) Ferritins, 48, 80000 and $9Fe_3O_4{\cdot}Fe(NO_3)_3$, respectively

(D) Ferritins, 24, 4500, and $8FeO(OH){\cdot}FeO(H_2PO_4)$, respectively

39. The correct statements regarding berylocene is

(i) It is an 18-π aromatic compound.
(ii) Both $C_5H_5^-$ rings are at equal distance from beryllium.
(iii) Both $C_5H_5^-$ rings are not at equal distance from beryllium.
(iv) It is an ionic compound.

(A) (i) and (iii)

(B) (ii) and (iv)

(C) (ii) and (iii)

(D) (iii) and (iv)

40. Two fragments are isolobal to each other, if their frontier orbitals

(i) are same in number
(ii) possess same symmetry
(iii) possess similar electron occupancy
(iv) exhibit same radial extent

The correct statements are

(A) (i) – (iv)

(B) (i), (ii) and (iii)

(C) (i) and (ii)

(D) (iii) and (iv)

41. If two octahedral metal clusters are fused through (i) vertex (ii) edge or (iii) face, the total electron count for the resultant polyhedra respectively, are

(A) 154, 138, 124

(B) 154, 136, 118

(C) 172, 160, 136

(D) 170, 168, 166

42. The ammonolysis of sulphur monochloride either in solution in an inert solvent or heated over solid ammonium chloride, yields **X** which upon reduction with metallic potassium or sodium azide yields **Y**. The products **X** and **Y**, respectively, are

(A) $[S_4N_4Cl_2]$, $[S_4N_4]$

(B) $[S_4N_4]$, $[S_4N_4Cl_2]$

(C) $[S_3N_3Cl_2]$, $[S_3N_3]^-$

(D) $[S_4N_4]$, $[S_3N_3]$

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43. A non-stoichiometric sample of iron oxide has the formula, Fe_xO. If the molar ratio of iron in the +3 and +2 oxidation states in this sample, $\frac{Fe^{3+}}{Fe^{2+}} = 0.01$, the value of x is:

(A) 1.005 (B) 1.0

(C) 0.995 (D) 0.985

44. When a crystal with a primitive cubic lattice undergoes a crystallographic phase transition, the (111) X-ray diffraction peak shifts from $\theta = 22^\circ$, to $\theta = 20^\circ$. What is the % change in the unit cell volume associated with the phase transition?

(A) – 24% (B) – 9%

(C) +24% (D) + 31%

45. A polymer sample has the following distribution of molecular weights:

Number of molecules	10	13	20	13
Molecular weight /10^4	35	40	45	50

The number average and weight average molecular weights of the polymer are respectively:

(A) 14.0, 42.5×10^4 (B) 43.2×10^4, 43.8×10^4

(C) 42.5×10^4, 43.5×10^4 (D) 43.2×10^4, 43.2×10^4

46. At 1000 K, which rotational transition for $H^{35}Cl$ would demonstrate maximum intensity? (rotational constant B = 10.595 cm^{-1})

(A) $J = 2$ to $J = 3$ (B) $J = 3$ to $J = 4$

(C) $J = 4$ to $J = 5$ (D) $J = 5$ to $J = 6$

47. The heat capacity of a systems with energy levels, $\epsilon_m = m^2\alpha$, where $m = 0,1,2,\ldots\ldots\infty$ and α is a constant, is given by

(A) $\frac{1}{2}Nk$ (B) $N\alpha$

(C) $\frac{1}{2}N\alpha$ (D) $N\alpha k$

48. The reaction, $2NO + O_2 = 2NO_2$ proceeds through the following steps:

$$2NO \rightleftharpoons N_2O_2$$
$$N_2O_2 + O_2 \rightarrow 2NO_2$$

If ΔG^0 for the first step is -15 kcal mol^{-1} and activation energy for the second step is 9 kcal mol^{-1}, the ratio k(35 °C)/k(25 °C), with k representing the overall rate constant, is given by

(A) 0.82 (B) 0.72

(C) 0.62 (D) 0.52

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49. The rate constant of a gas phase reaction at 300 K is doubled when the pressure is increased from 1 to 2000 atm. The volume change on activation ($\Delta V^{\ddagger}$) is given by,

(A) - 6.5 mL mol^{-1}	(B) - 7.5 mL mol^{-1}
(C) - 8.5 mL mol^{-1}	(D) - 9.5 mL mol^{-1}

50. The first two lines in the R-branch of the vibrational spectrum of HCl appear at 2900 cm^{-1} and 2924 cm^{-1}. The first line in the R-branch of DCl spectrum appears at 2090 cm^{-1}. The second line in the latter is expected to appear at

(A) 2094 cm^{-1}	(B) 2096 cm^{-1}
(C) 2098 cm^{-1}	(D) 3002 cm^{-1}

51. The bond length (r_{CO}) in CO_2 is 1.2Å. The moment of inertia of CO_2 would be close to ($m_C = 2.0 \times 10^{-26}$ kg and $m_O = 2.7 \times 10^{-26}$ kg)

(A) 3.9×10^{-46} kg m^2	(B) 6.0×10^{-46} kg m^2
(C) 7.8×10^{-46} kg m^2	(D) 9.8×10^{-46} kg m^2

52. The wave function of the ground electronic state of a H-atom in spherical polar (r, θ,Φ) coordinates is given by $\Psi(r) = Ne^{-\alpha r}$ (α is a constant and $0 \leq r \leq \infty$, $0 \leq \theta \leq \pi$, $0 \leq \Phi \leq 2\pi$). The constant N equals to

(A) $(1/\pi\alpha^3)^{1/2}$	(B) $(\alpha^3/\pi)^{1/2}$
(C) $(\pi/\alpha^3)^{1/2}$	(D) $(\pi\alpha^3)^{1/2}$

53. Calculate the change in entropy of 2 mols of an ideal gas upon heating from a volume of 100 litres at 323 K to a volume of 150 litres at 423 K. ($C_V = 7.88$ cal K^{-1} mol^{-1})

(A) 34.23 JK^{-1}	(B) 44.63 JK^{-1}
(C) 64.53 JK^{-1}	(D) 24.53 JK^{-1}

54. The uncertainty product, $\Delta x \Delta p_x$, in the ground state of one dimensional harmonic oscillator is

(A) greater than $h/_{2\pi}$	(B) equal to $h/_{2\pi}$
(C) less than $h/_{4\pi}$	(D) equal to $h/_{4\pi}$

55. Collision theory depends on knowing the fraction of total number of molecules having at least the threshold energy, E_a. When E_a = 10 kJ mol^{-1}, the increase in percentage of this fraction on increasing the temperature from 200 K to 210 K is closest to

(A) 67	(B) 57
(C) 35	(D) 47

---**End**---