P-64

ENTRANCE EXAMINATION – 2017

Ph. D. Chemistry

TIME: 2 HOURS **MAXIMUM MARKS: 80**

HALL TICKET NUMBER: [ ]

INSTRUCTIONS

1. Write your **HALL TICKET NUMBER** in the space provided above and also on the **OMR** ANSWER SHEET given to you.
2. Make sure that pages numbered from **1 - 21** are present (excluding 5 pages assigned for rough work).
3. There are eighty (80) multiple choice questions in this paper (**20 in Part-A** and **60 in Part-B**). You are required to answer all **questions of Part-A** and a **maximum of 20 questions of Part-B**. If more than the required numbers of questions are answered, **only the first 20 questions of Part-B** will be evaluated.
4. Each question in Part-A and Part-B carries **two marks**.
5. **There is negative marking** for both Part-A and Part-B. **Each wrong answer carries –0.66 mark.**
6. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
7. Hand over the OMR answer sheet to the invigilator at the end of the examination.
8. In case of a tie, the marks obtained in the first 20 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. OMR 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 = 6.625×10^{-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} = 0.082 L atm 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} N m^{-2}; RT/F (at 298.15 K) = 0.0257 V.

Part-A

1. 500 mL of an aqueous solution of AgCl contains 0.10 mg of Ag^{+} ions. The concentration of Cl^{-} ions in the solution is [K_{sp} (AgCl) = 1.0×10^{-10} M^2 ; atomic weight of Ag = 107.9 g/mol]

   [A] 1.0×10^{-10} M [B] 5.4×10^{-5} M

   [C] 9.2×10^{-4} M [D] 1.0×10^{-4} M

2. 34.76 mL of $KMnO_4$ solution of unknown strength is needed for the titration of 62.50 mL of 0.20 M $Na_2C_2O_4$ solution. The normality of $KMnO_4$ solution is

   [A] 0.36 [B] 0.56

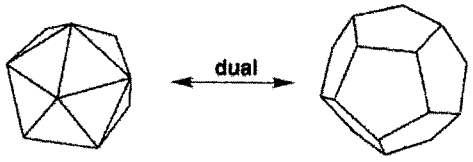
   [C] 0.72 [D] 0.18

3. An icosahedron can be described as bicapped

   [A] hexagonal antiprism [B] pentagonal prism

   [C] pentagonal antiprism [D] hexagonal prism

4. Which of the following remains unchanged in the geometrical conversion?



Icosahedron Dodecahedron

[A] Number of vertices [B] Number of edges

[C] Number of faces [D] All of the above

5. Among the following set of quantum numbers, which one represents an electron with highest energy?

[A] n=3, l=0, m_l=0, m_s=-1/2 [B] n=3, l=1, m_l=-1, m_s=-1/2

[C] n=4, l=0, m_l=0, m_s=+1/2 [D] n=3, l=2, m_l=0, m_s=+1/2

6. For which of the following species is the color not due to a d-d transition? VO^{2+}, CrO_4^{2-}, MnO_4^{2-}, MnO_4^-

[A] MnO_4^{2-} and MnO_4^- [B] VO^{2+} and MnO_4^-

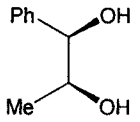
[C] CrO_4^{2-} and MnO_4^- [D] MnO_4^{2-} and CrO_4^{2-}

7. When 2-butyne is subjected to hydrogenation with Pd-$BaSO_4$/quinolone, the product formed is:

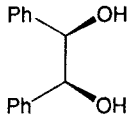
[A] *n*-butane [B] *cis*-2-butene

[C] *trans*-2-butene [D] 1-butene

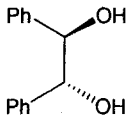
8. Identify the *meso* compound from the following:



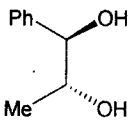
[A]



[B]



[C]



[D]

9. The metal complex that is generally used in the tanning of leather is that of

[A] Rhodium [B] Chromium

[C] Ruthenium [D] Tungsten

10. Who won the Nobel prize for outstanding contribution to the chemistry of carbocations?

[A] H. C. Brown [B] G. A. Olah

[C] E. J. Corey [D] R. B. Woodward

11. Identify the most appropriate rule in an asymmetric Grignard reaction of prochiral ketone:

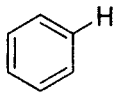
[A] Hückel rule [B] Cram's rule

[C] Baldwin's rule [D] Hoffmann's rule

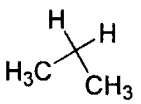
12. Arrange the following molecules in the increasing order of C-H bond dissociation energy (kJ mol^{-1}).

(I)

(II)



(III)



(IV)

[A] IV<II<III<I [B] I<III<IV<II

[C] III<II<IV<I [D] II<IV<I<III

13. The property of two systems that should be equalized for chemical equilibrium is

[A] entropy [B] chemical composition

[C] chemical potential [D] enthalpy

14. A molecule will be chiral **only** if it lacks:

[A] center of inversion [B] reflection plane

[C] proper axis of rotation [D] improper axis of rotation

15. The average momentum of a particle confined in a one-dimensional box of length L is

[A] 0 [B] $\frac{n\pi\hbar}{L}$

[C] $\frac{n^2h^2}{4L^2}$ [D] $\frac{n^2\hbar^2}{4L^2}$

16. A molecule that will show pure rotational spectrum is

[A] ethylene [B] allene

[C] *cis* butadiene [D] *trans* butadiene

17. The molecule with the largest rotational partition function at a given temperature, among the following is

[A] $H-C\equiv C-H$ [B] $CH_3-C\equiv C-H$

[C] $CH_3-C\equiv C-CH_3$ [D] $Cl-C\equiv C-Cl$

18. The mean value of a set of numbers can be given as arithmetic mean (AM), geometric mean (GM) and harmonic mean (HM). Which of the following correctly describes the relation among these three?

[A] $AM \leq GM \leq HM$ [B] $GM \leq AM \leq HM$

[C] $HM \leq GM \leq AM$ [D] $HM \leq AM \leq GM$

19. A 230 m long train running at a speed of 50 km h^{-1} crosses another train running in the opposite direction at a speed of 50 km h^{-1} in 18 seconds. What is the length of the other train?

[A] 270 m [B] 330 m

[C] 250 m [D] 230 m

20. The most important peaks in the electron impact mass spectrum of 2-pentanone will be at the m/z values of :

(A) 15, 29, 43, 58, 71, 86 (B) 15, 29, 43, 57, 71, 86

(C) 15, 29, 43, 71, 86 (D) 15, 29, 57, 71, 86

Part-B

21. The resistance of 0.2 M solution of an electrolyte is 50 Ω and its specific conductance is 1.3 S m^{-1}. If the resistance of the 0.4 M solution of the same electrolyte is 260 Ω, the difference in molar conductance of the two solutions is

[A] 5.875 x 10^{-3} S m^2 mol^{-1} [B] 0.25 x 10^{-3} S m^2 mol^{-1}

[C] 6.25 x 10^{-4} S m^2 mol^{-1} [D] 6.5 x 10^{-4} S m^2 mol^{-1}

22. The metal-metal bond orders in $[Re_2Cl_8]^{4-}$, $[Re_2Cl_8]^{2-}$ and $[Re_2Cl_6(PPh_3)_2]$ are respectively

[A] 3, 4 and 4 [B] 4, 3 and 2

[C] 3, 2 and 2 [D] 2, 3 and 4

23. Which of the molecules/ions has/have an S_4 axis?

[A] PF_5 and SO_4^{2-} [B] SF_4 and SO_4^{2-}

[C] SO_4^{2-} only [D] BF_3 and SF_4

24. Choose the correct statement/s in connection with iodometric titrations in the presence of excess iodide solution:
(i) The reactive species in these titrations is the triodide anion
(ii) Starch solution is added in the beginning of the titration as an indicator.
(iii) The titration can be performed in the presence of stannous chloride.

[A] (i) and (ii) [B] (ii) and (iii)

[C] (i) and (iii) [D] (i) only

25. The ground state term symbol for Ho^{3+} (Atomic number = 67) ion is

[A] $^5I_8$ [B] $^5H_{15/2}$

[C] $^4I_{15/2}$ [D] $^2F_{7/2}$

26. The hapticities (i.e. 'n' value in η^n) of the Cp^- (cyclopentadienide) rings in the 18-electron compound $Cp_2W(CO)_2$ are

[A] 1, 3 [B] 3, 5

[C] 2, 4 [D] 4, 5

27. The origin of yellow-orange color of $[Co(en)_3]^{3+}$ (en = 1, 2-diaminoethane) is

[A] ligand-field transition [B] ligand-to-metal charge transfer

[C] metal-to-ligand charge transfer [D] intraligand transition

28. The number of hydrophilic and hydrophobic channels in **Ferritin** are respectively

[A] 8, 8 [B] 6, 6

[C] 8, 6 [D] 6, 8

29. The half-life of ^{32}P is 14.2 days. How long would it take for the disintegration to reduce from 42,000 per minute to 500 per minute?

[A] 90.8 days [B] 39.42 days

[C] 14.19 days [D] 1.33 days

30. Formulae for ortho-, pyro-, chain-, and double chain silicates are respectively

[A] $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[Si_2O_3]^{2-}$, $[Si_4O_{11}]^{6-}$ [B] $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[SiO_3]^{2-}$, $[Si_4O_{11}]^{6-}$

[C] $[SiO_4]^{4-}$, $[Si_2O_7]^{4-}$, $[SiO_3]^{3-}$, $[Si_4O_{11}]^{6-}$ [D] $[SiO_4]^{4-}$, $[Si_2O_6]^{6-}$, $[SiO_3]^{2-}$, $[Si_4O_{12}]^{6-}$

31. The intercept of the Tafel plot (η vs. log (i)) is used to estimate

[A] Transfer coefficient [B] Rate of the reaction

[C] Exchange current density [D] Kinetic current density

32. The metalloenzymes/ metalloproteins, associated with the metals Fe, Zn, Mo and Cu are

[A] hemocyanin, ferritin, sulfite oxidase and carboxypeptidase respectively.

[B] ferritin, carbonic anhydrase, sulfite oxidase and hemocyanin respectively.

[C] ferritin, aldehyde oxidase, nitrogenase and vitamin B12 respectively.

[D] hemoglobin, sulfite oxidase, carbonic anhydrase and blue protein respectively

33. The total number of lines observed in the ESR spectrum of naphthalenide ion (I = 1/2 for proton) is

[A] 5 [B] 25

[C] 9 [D] 15

34. Which of the following pair of complex ions are expected to undergo tetragonal distortion?

[A] $[Cr(H_2O)_6]^{2+}$ and $[Cu(NH_3)_6]^{2+}$ [B] $[Fe(CN)_6]^{4-}$ and $[MnF_6]^{4-}$

[C] $[Cr(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ [D] $[MnF_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$

35. 0.5582 g of iron ore is converted into Fe_2O_3. Weight of Fe_2O_3 obtained is 0.2481 g. The percentage of iron (Fe) in the ore is (Atomic weight of Fe = 55.85 g/mol)

[A] 31.09 [B] 7.77

[C] 34.97 [D] 44.44

36. The ***styx*** number of B_4H_{10} is

[A] 2002 [B] 4120

[C] 4012 [D] 4220

37. The redox indicator among the following is:

[A] Methyl red [B] Ferroin

[C] Fluorescein [D] Phenolphthalein

38. The percentage of iron in +3 oxidation state in $Fe_{0.9}O$ is close to

[A] 22.22 [B] 84.20

[C] 28.59 [D] 18.49

39. A 100 mL buffer solution of pH 7 contains 10 mmol of the acid HA (pK_a = 7.00), and 10 mmol of the conjugate base A^-. To this solution, 1.0 mmol of solid NaOH is added. The pH of the resulting solution is

[A] 7.00 [B] 12.00

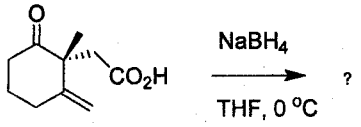
[C] 7.09 [D] 6.5

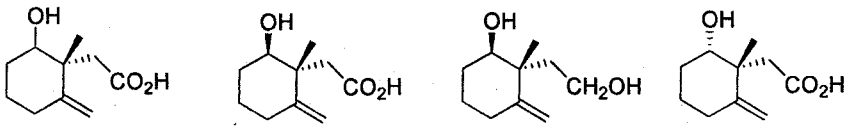
40. Among the following, the EPR active species is

[A] Oxy-hemocyanin [B] Cytochrome

[C] Chlorophyll [D] Caboxypeptidase

41. Predict the product in the following reaction:





[A] [B] [C] [D]

42. Second order spectra in ^{1}H-NMR occur due to

[A] weakly coupled protons [B] strongly coupled protons

[C] high field machines [D] spatially close protons

43. Which of the following is the correct order of increasing molecular ion lifetime?

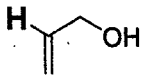
[A] alcohols < ketones < unbranched hydrocarbons < aromatic compounds

[B] alcohols < unbranched hydrocarbons < aromatic compounds < ketones

[C] ketones < alcohols < unbranched hydrocarbons < aromatic compounds

[D] unbranched hydrocarbons < alcohols < ketones < aromatic compounds

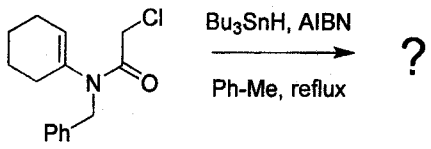
44. The splitting pattern of the hydrogen (marked bold) in the ^{1}H NMR spectrum of the following compound is:

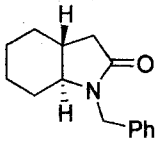


[A] quint [B] ddt

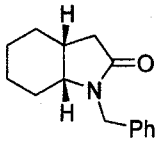
[C] tdd [D] tt

45. Predict the most probable product in the following transformation.





[A]



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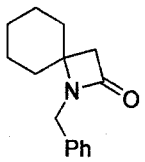
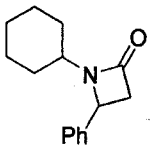
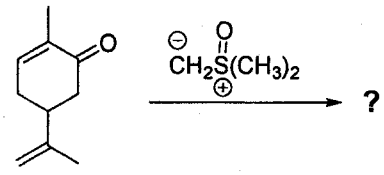


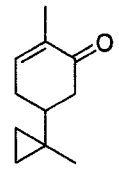
[C]



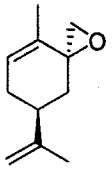
[D]

46. The major product formed in the following reaction is:





[A]



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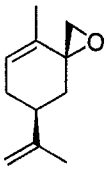
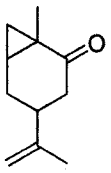
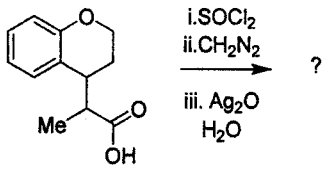


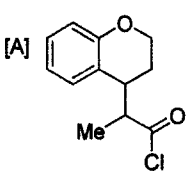
[C]

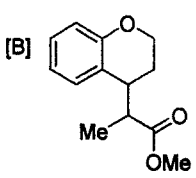


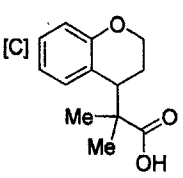
[D]

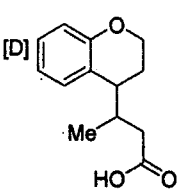
47. The product formed in the following reaction is



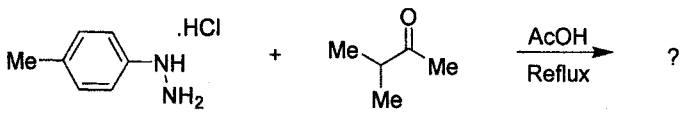


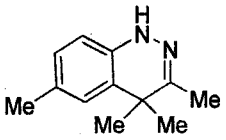


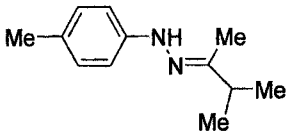


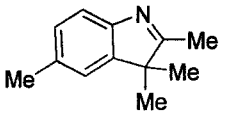


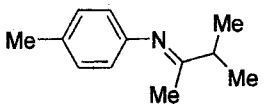
48. Identify the most appropriate product in the following reaction.



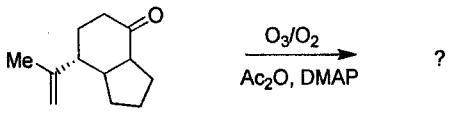
[A] 

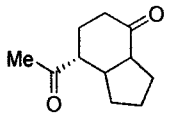
[B] 

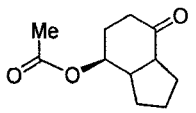
[C] 

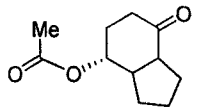
[D] 

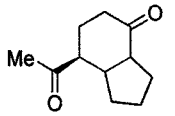
49. Predict the product in the following reaction.



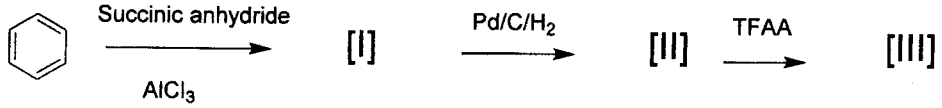
[A] 

[B] 

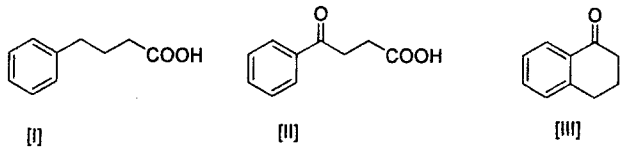
[C] 

[D] 

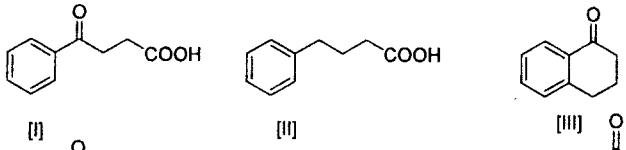
50. Identify the product in the following reaction sequence:



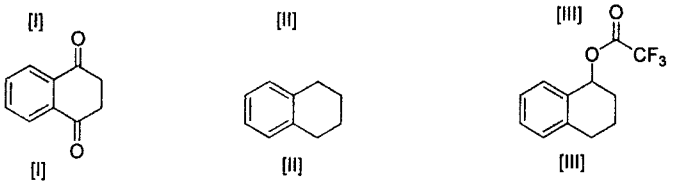
[A]



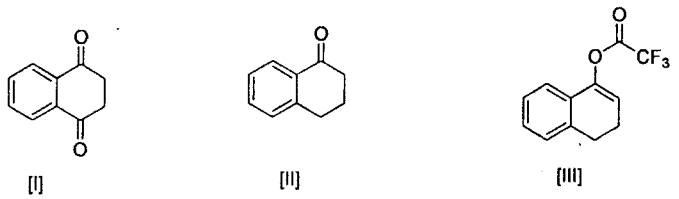
[B]



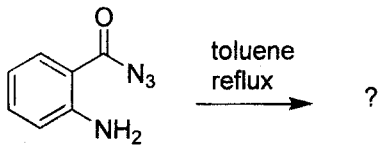
[C]

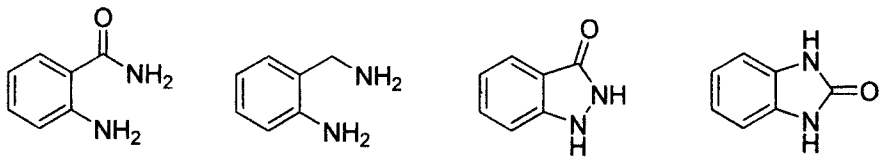


[D]



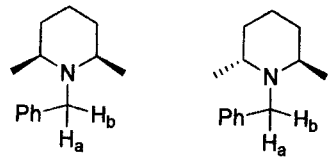
51. Identify the product in the following reaction.





[A] [B] [C] [D]

52. The "topicity" of the two benzylic protons (H_a, H_b) in the compounds I and II is:



(I) (II)

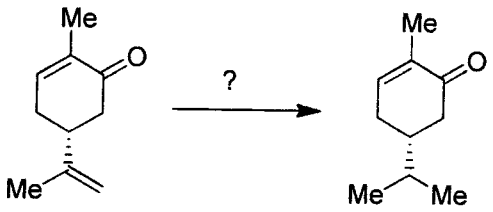
[A] Enantiotopic in both I & II

[B] Diastereotopic in both I & II

[C] Diastereotopic in I & enantiotopic in II

[D] Diastereotopic in II & enantiotopic in I

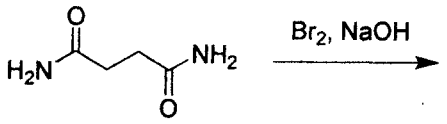
53. Identify the most appropriate reagent for the following transformation:

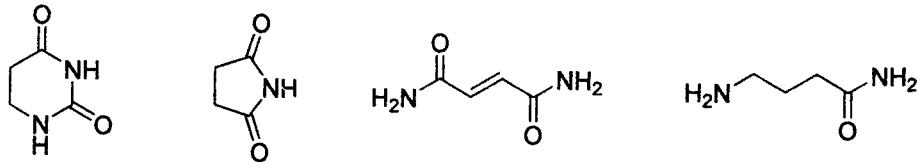


[A] H_2, $Rh(PPh_3)_3Cl$ [B] H_2, Pd-C

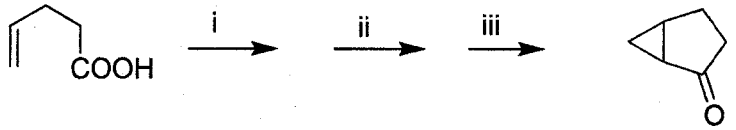
[C] Li/liq-NH_3 [D] $LiAlH_4$

54. The major product obtained in the following transformation is:





55. The suitable reagent system for the following transformation is:



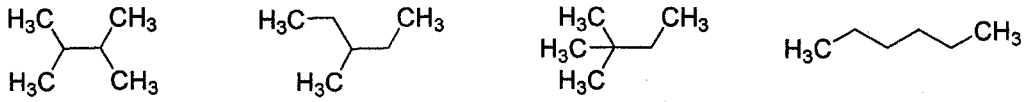
[A] i. $SOCl_2$; ii. CH_2N_2; iii. $Rh_2(OAc)_4$

[B] i. CH_2N_2; ii. $SOCl_2$; iii. $Rh_2(OAc)_4$

[C] i. $BF_3.Et_2O$; ii. CH_2N_2; iii. $Rh_2(OAc)_4$

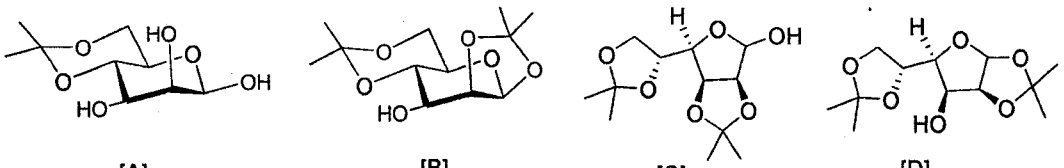
[D] i. CH_2N_2; ii. $BF_3.Et_2O$; iii. $Rh_2(OAc)_4$

56. A hydrocarbon with the formula C_6H_{14} gives a mixture containing only two monochlorides in photochemical chlorination. One of these compounds solvolyzes very rapidly in ethanol, whereas the other solvolyzes very slowly. The hydrocarbon is:



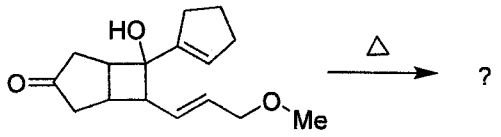
[A] [B] [C] [D]

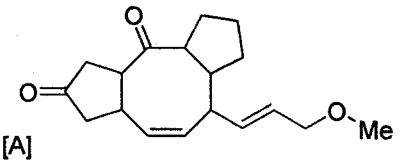
57. D-Mannose upon reaction with I_2 and acetone at room temperature for 24 h provides:

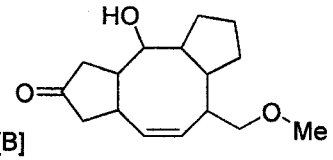


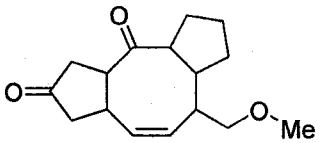
[A] [B] [C] [D]

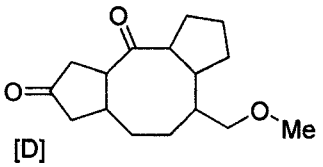
58. The product of the following reaction is:



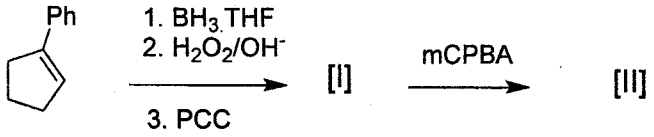
[A]


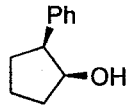
[B]


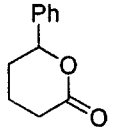
[C]


[D]


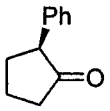
59. The products formed in the following reaction are:

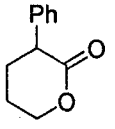


[A]


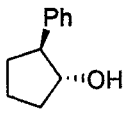
[I]


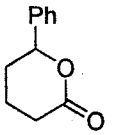
[II]

[B]


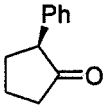
[I]


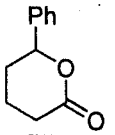
[II]

[C]


[I]


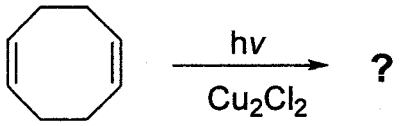
[II]

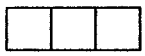
[D]


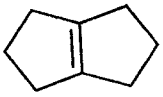
[I]


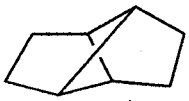
[II]

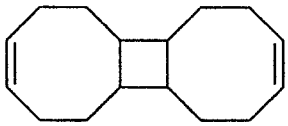
60. The major product formed in the following reaction is:



[A] 

[B] 

[C] 

[D] 

61. 1.0 mol of a diatomic perfect gas at 200 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Its molar heat capacity $C_{v,m}$ = 27.5 J $K^{-1}mol^{-1}$. The work done (w), internal energy change (ΔU) and enthalpy change (ΔH) in kJ, respectively are

[A] - 2.75, + 2.75, - 3.58

[B] + 2.75, + 2.75, + 3.58

[C] + 2.75, - 2.75, 0.00

[D] + 27.5, 0.00, + 35.8

62. The equilibrium constant for the gas phase isomerization A ⇌ B at 500 K is 0.4. A mixture of 10.0 g of A and 20.0 g of B is heated to 500 K in a closed vessel. The mass of A at equilibrium is

[A] 21.4 g

[B] 20.0 g

[C] 18.0 g

[D] 12.3 g

63. For a second order reaction, A → products, if the initial concentration of A is $[A]_0$ and the amount reacted at time t is x, a linear plot against t is obtained for

[A] $[A]_0 - 2x$ [B] $\frac{1}{[A]_0 - x}$

[C] $\frac{x}{[A]_0 - x}$ [D] $\ln([A]_0 - 2x)$

64. The X-ray diffraction peak for the (1 1 0) plane of a cubic lattice is observed at 2θ = 22.0°. The peak for the (1 2 1) plane will appear at a 2θ value of

[A] 38.6° [B] 24.2°

[C] 19.3° [D] 12.1°

65. The standard reduction potentials for $Cu^{2+}_{(aq)}|Cu_{(s)}$ and $Cu^{+}_{(aq)}|Cu_{(s)}$ are respectively, +0.34 V and +0.52 V. The standard Gibbs free energy change for the reaction, $2Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$ is

[A] + 15.44 kJ mol^{-1} [B] - 15.44 kJ mol^{-1}

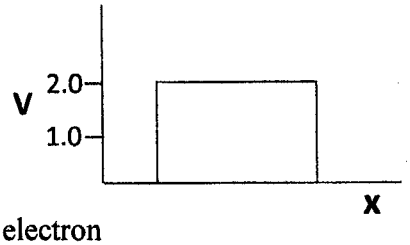
[C] + 34.74 kJ mol^{-1} [D] - 34.74 kJ mol^{-1}

66. The pair of observables that can be measured simultaneously with unlimited precision is

[A] p_x , p_y [B] J_x , J_y

[C] p_z , z [D] J_z , φ

67. The particle with the lowest tunnelling probability through the potential barrier shown below when all of them have 1.2 eV of kinetic energy is



[A] electron [B] proton

[C] neutron [D] α-particle

68. The mean activity coefficient of KCl at 0.01 M concentration is 0.90. The mean activity coefficient at 0.04 M concentration is close to

[A] 38.6 [B] 1.8

[C] 0.81 [D] 0.64

69. The molecule having C_2 symmetry element among the following is

[A] NH_3 [B] CH_4

[C] CH_3Cl [D] CH_3NH_2

70. The IR active mode of acetylene among the following is (the arrows indicate the direction of atomic displacements)

[A] $\leftarrow H-C\equiv C-H\rightarrow$ [B] $\overset{\uparrow}{H}-C\equiv C-\underset{\downarrow}{H}$

[C] $\underset{\downarrow}{H}-C\equiv C-\underset{\downarrow}{H}$ [D] $H\overset{\leftarrow}{-}C\equiv C\overset{\rightarrow}{-}H$

71. Microwave spectrum of $H^{35}Cl$ shows a series of equally spaced lines separated by 6.26×10^{11} Hz. If the reduced mass of $H^{35}Cl$ is 1.63×10^{-27} kg, the bond length of $H^{35}Cl$ would be

[A] 0.91 Å [B] 1.28 Å

[C] 2.27 Å [D] 1.61 Å

72. The de Broglie wave length of an electron that has been accelerated through a potential difference of 100 V will be

[A] 0.23 nm [B] 2.1 nm

[C] 1.3 nm [D] 0.123 nm

73. The average energy at temperature T of a system having an ensemble of N identical particles (indistinguishable), where each particle can have only two energy levels 0 and $h\nu$ is [$k_BT = \beta$]

[A] $Nh\nu$ [B] ½ $Nh\nu$

[C] $\frac{Nh\nu}{e^{\beta h\nu}+1}$ [D] $\frac{N}{e^{\beta h\nu}+1}$

74. The Maxwell's relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ results from

[A] dU = dQ – dW [B] dH = dU + PdV + VdP

[C] dA = dU – TdS – SdT [D] dG = dH – TdS – SdT

75. $\int sin^5 x\, dx =$

[A] - 1/5 $\cos^5 x$ + 2/3 $\cos^3 x$ – cos x + c

[B] - 5 $\cos^5 x$ + 3 $\cos^3 x$ – cos x + c

[C] - 5 $\cos^5 x$ + 2 $\cos^3 x$ – cos x + c

[D] 1/5 $\cos^5 x$ - 2/3 $\cos^3 x$ + cos x + c

76. The net charge of a protein below the isoelectric point, above the isoelectric point and at the isoelectric point are, respectively,

[A] – 1, 0, + 1 [B] + 1, 0, - 1

[C] – 1 , + 1, 0 [D] + 1, - 1, 0

77. The number of vibrational normal modes of $CH_3 - CH_2 - CH_3$ is:

[A] 29 [B] 28

[C] 27 [D] 26

78. The vibrational frequency of a first order saddle point is identified with

[A] a small negative number [B] a small positive number

[C] a large positive number [D] an imaginary number

79. The ionization energy for hydrogen atom is 13.6 eV. The ionization energy for the ground state of Li^{2+} is approximately

[A] 27.2 eV [B] 40.8 eV

[C] 54.4 eV [D] 122.4 eV

80. Which of the following is not a Hermitian operator?

[A] x [B] $i\frac{d}{dx}$

[C] $\frac{d^2}{dx^2}$ [D] $i\hbar\frac{d^2}{dx^2}$

**********END**********